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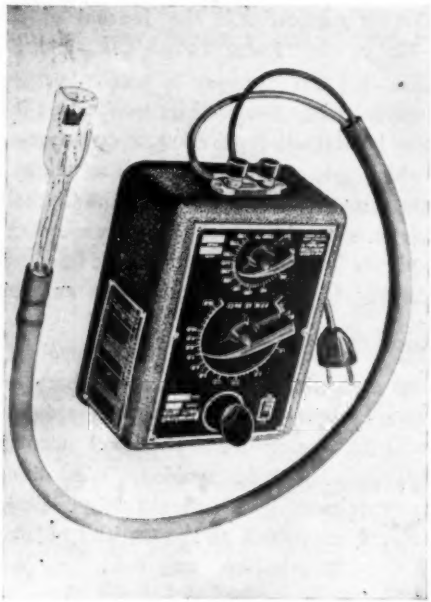

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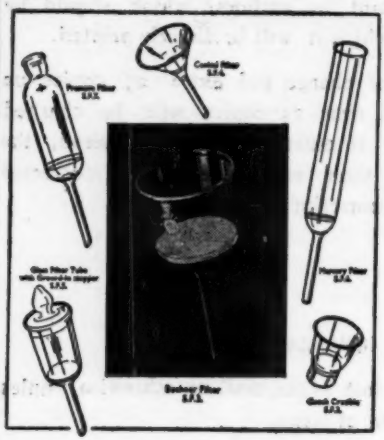

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ACHARYA JAGADISH CHANDRA BOSE BIRTH CENTENARY

The birth centenary of Acharya Jagadish Chandra Bose falls on the 30th November, 1958. A Committee, of which I am the President, has been formed to celebrate the centenary in a manner befitting the occasion. Jagadish Chandra's contributions to the scientific and cultural renaissance of this country were many-sided and fruitful.

The programme of the centenary celebration includes, amongst others, the following important items :

I. ***Publications*** :

(a) Biography of J. C. Bose in English, Bengali and if possible, in other regional languages,

(b) Publication of a memorial volume of the Transactions of the Bose Institute founded by Jagadish Chandra in 1918.

II. ***Lectures and Seminars*** :

On recent progress in Science, specially on subjects in which Jagadish Chandra had made important contributions.

III. ***Exhibition and Demonstrations*** :

(i) Letters, manuscripts and other important documents associated with the life and activities of Jagadish Chandra.

(ii) Scientific apparatus invented by Jagadish Chandra for his investigations; actual working of some of these historical apparatus will be demonstrated.

IV. ***Documentary Film*** :

On the life and activities of Jagadish Chandra. The issue of commemoration postage stamps.

V. ***Creation of Endowment Funds*** :

(a) For visiting Professorships.

(b) There is also a proposal for associating the name of Jagadish Chandra with a programme for encouraging greater participation in science amongst the youth of this country.

The Government of India has agreed to undertake the preparation of documentary film and the issue of commemorative postage stamps. In addition, a Government of India contribution to the Endowment Fund probably of Rupees one lakh towards V(a) may be expected.

The Working Committee has estimated that for implementing items I to III of the programme at least another Rupees one lakh and a half will be necessary.

If the scheme V(b) materializes, additional funds will be necessary. Any balance left after the celebration is over, will be credited to the Endowment Fund.

I make an earnest appeal to the general public to come forward with generous contributions to commemorate the birth centenary of this great son of India.

Sd. BIDHAN CHANDRA ROY
President

One hundred years ago, in 1858, Acharya Jagadish Chandra Bose was born. This year, on the 30th November, his birth centenary will be observed, for which preparations are being made.

A centenary celebration committee, consisting of eminent personalities, has been formed to celebrate the historic occasion. The committee is functioning in close co-operation with the Bose Institute of which Acharya Jagadish Chandra Bose was the Founder. This national institution, which embodies the late Acharya's mission of advancement of knowledge by research and its diffusion by discourses and demonstrations, will also celebrate its Founder's birth centenary.

The centenary celebration committee will arrange to observe the centenary week during which meetings, exhibitions and lectures will be held. Distinguished visitors from all over the country as well as from foreign lands will attend the meetings.

To carry out the programme effectively large funds would be necessary.

Donors who are interested in the permanent programme are requested to contribute their donations to the Bose Institute, 93/1, Upper Circular Road, Calcutta-9.

Donors interested in the centenary week are requested to send their donations to the Treasurer, Acharya Jagadish Chandra Bose Birth Centenary Committee at the same address.

Sd. S. K. MITRA
Secretary
Acharya Jagadish Chandra Bose
Birth Centenary Committee
June 20, 1958

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[Jour. Indian Chem. Soc., Vol. 35, No. 7, 1958]

STUDIES IN THE MICHAEL CONDENSATION. PART II. SYNTHESES OF 5-METHYL- AND 1:5-DIMETHYL-BI*cyclo*-0:3:4-NONANE-2:4-DIONES

By Amalendu Banerjee and Bidyut Kamal Bhattacharyya

Methyl 2-keto-3-methyl-3-carbomethoxy-*cyclo*hex-$\Delta^{1:6}$-enylacetate on hydrolysis yields 2-keto-3-methyl*cyclo*hex-$\Delta^{1:6}$-enylacetic acid. The methyl ester of the acid on condensation with either diethyl malonate or ethyl cyanoacetate, followed by hydrolysis, esterification, the Dieckmann cyclisation and decarboxylation, affords 5-methylbi*cyclo*-0:3:4-nonane-2:4 dione. Methylation of either methyl 2-keto-3-methyl-6-(diethyl malonate)-*cyclo*hexylacetate or methyl 2-keto-3-methyl-6-(ethyl cyanoacetate)-*cyclo*hexylacetate, followed by hydrolysis, esterification, the Dieckmann reaction and decarboxylation, furnishes 1:5-dimethylbi*cyclo*-0:3:4-nonane-2:4-dione.

The Michael condensation between diethyl malonate and an $\alpha\beta$-unsaturated alicyclic ketone has been studied by Bartlett and Forrest Woods (*J. Amer. Chem. Soc.*, 1940, **62**, 2933) and Mukherjee (this *Journal*, 1948, **25**, 155). In the following is described the synthesis of the bi*cyclo*-0:3:4-nonane derivatives* by the application of the Michael reaction.

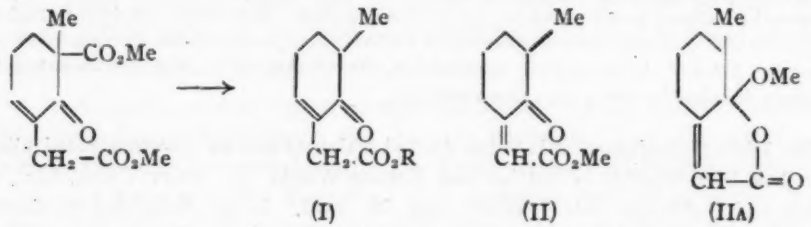
The hydrolysis and decarboxylation of methyl 2-keto-3-methyl-3-carbomethoxy-*cyclo*hex-$\Delta^{1:6}$-enylacetate (Sen Gupta and Bhattacharyya, this *Journal*, 1954, **31**, 337) with hydrochloric acid afforded a crystalline acid (λ_{max} 236 mμ ; log ϵ 3.84), which on esterification furnished the methyl ester (λ_{max} 230 mμ ; log ϵ 3.85). The absorption maxima clearly indicate that the structures of the acid and its ester are represented by (I: R=H and R=Me). But the treatment of the afore-mentioned substituted β-keto ester with alkali gave an acidic material which could not be crystallised. This acidic material, on esterification, furnished a methyl ester. The ultraviolet absorption of this ester (λ_{max} 220 mμ ; log ϵ 3.61) indicates that the major component may be represented either by the structure (II) (Shen and Whiting, *J. Chem. Soc.*, 1950, 1772) or (IIA) (Shaw, *J. Amer. Chem. Soc.*, 1946, **68**, 2510). The inflection at 229-232 mμ (log ϵ 3.55) shows also the presence of the isomeric unsaturated keto-ester (I: R=Me) in the mixture.

The condensation of diethyl malonate with the unsaturated keto-ester (I: R=Me) was performed according to Mukherjee (*loc.cit.*) to yield methyl 2-keto-3-methyl-6-(diethyl malonate)-*cyclo*hexylacetate (III: R=Me ; R_1=H ; R_2=CO_2Et ; R_3=Et), which, on methylation with methyl iodide and sodium either in alcohol or in benzene, afforded the methylated compound (III: R=R_1=Me ; R_2=CO_2Et ; R_3=Et). In order to separate easily the unmethylated ester from the methylated product, the Michael condensation was performed with ethyl cyanoacetate to afford methyl 2-keto-3-methyl-6-(ethyl cyanoacetate)-*cyclo*hexylacetate which, on treatment with methyl iodide and alcoholic sodium ethoxide, furnished (III: R=R_1=Me ; R_2=CN ; R_3=Et).

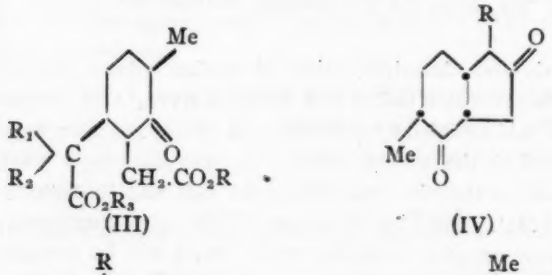
* A preliminary report appeared in the *Science & Culture*, 1956, **21**, 549.

The compounds (III : R=Me ; R_1=H ; R_2=CO_2Et ; R_3=Et and R=Me ; R_1=H ; R_2=CN ; R_3=Et), on treatment with acid, followed by esterification, afforded dimethyl 2-keto-3-methyl*cyclo*hexane-1 : 6-diacetate. The latter, on cyclisation with sodium methoxide in benzene, followed by hydrolysis and decarboxylation of the resulting β-keto ester with acid, afforded 5-methylbi*cyclo*-0 : 3 : 4-nonane-2 : 4-dione (IV : R=H). It may be mentioned that the dicarboxylic acid (III : R=R_1=R_2=R_3=H), on pyrolysis with lead carbonate, did not furnish any desired dione.

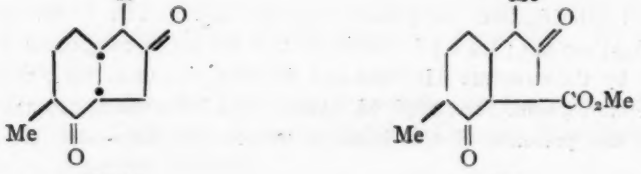
The methylated esters (III : R=R_1=Me ; R_2=CO_2Et ; R_3=Et and R=R_1=Me ; R_2=CN ; R_3=Et), when subjected to the same sequence of reactions as described above, afforded, through the β-keto ester (V), 1 : 5-dimethylbi*cyclo*-0 : 3 : 4-nonane-2 : 4-dione.



(I) (II) (IIA)



(III) (IV)



(IVA) (V)

The stereochemistry of 1 : 5-dimethylbi*cyclo*-0 : 3 : 4-nonane-2:4-dione is probably represented either by (IV) with *cis* ring-fusion (Hückel *et al.*, *Annalen*, 1935, **518**, 155 ; Barton, *Experientia*, 1950, **6**, 316 ; Johnson, *ibid*, 1951, **7**, 315) and with the methyl group at C_1 on the β-side, because inspection of the model reveals a considerable non-bonded interaction between the methyl group on the α-side and axial hydrogen atom at C_6, or (IVA).

EXPERIMENTAL

All m.p's and b.p's. are uncorrected. The U.V. absorption spectrum was determined in 95% ethanol by the Unicam spectrophotometer, S.P. 500.

2-Keto-3-methylcyclohex-$\Delta^{1:6}$-enylacetic Acid (I: R=H).—(*a*). A mixture of methyl 2-keto-3-methyl-3-carbomethoxy*cyclo*hex-$\Delta^{1:6}$-enylacetate (14.4 g.) and 20% HCl (80 c.c.) was refluxed for 9 hrs. The reaction mixture was cooled and the precipitated oil was extracted five times with ether. The combined ethereal solution was washed with saturated sodium bicarbonate solution. The cooled alkaline solution was acidified with cold 20% HCl and the precipitated oil was thoroughly extracted with ether. The ethereal layer was washed once with a small quantity of water and dried over anhydrous sodium sulphate. After removal of the solvent, the crude acid (9.3 g.) was crystallised from a mixture of ether and petroleum ether (40-60°) to furnish a crystalline material (5.1 g), m.p. 89-92°. On concentration of the mother-liquor, another crop of crystals (2 g.), m.p. 90-91°, was obtained. The acid was crystallised three times from the same mixture of solvents to furnish the pure material, m.p. 95°; λ_{max} 236 mμ (log ϵ 3.84). (Found: C, 64.65; H, 7.09. $C_9H_{12}O_3$ requires C, 64.27; H, 7.18%).

(*b*). A mixture of the above substituted β-keto ester (4.8 g.), glacial acetic acid (10 c.c.) and 20% HCl (8 c.c.) was heated on the steam-bath for 2 hrs. The cold reaction mixture, after dilution with water and working up, furnished the acid (2.2 g.), m.p. 89-91°.

*Alkaline Treatment of Methyl 2-Keto-3-methyl-3-carbomethoxy*cyclo*hex-$\Delta^{1:6}$-enylacetate*.—The above substituted β-keto ester (12 g.) was refluxed with 10% aqueous NaOH (65 c.c.) for 3 hrs. A further quantity of alkali (20 c.c.) was added to the reaction mixture and the heating continued for 2 hours more. After cooling, the alkaline solution, containing a sweet smelling oil, was extracted with ether. The cooled aqueous alkaline solution was acidified with dilute HCl and the precipitated oil was worked up, as described before, to furnish a gummy residue (5 g.) which was refluxed with methanol (15 c.c.) and H_2SO_4 (1 c.c., *d* 1.84) for 30 hrs. The ester, after working up with ether and saturated sodium bicarbonate solution, was distilled to yield an oil (4.2 g.); b.p. 120-22°/2.5-3 mm, λ_{max} 220 mμ (log ϵ 3.61) with inflections at 226-228 mμ (log ϵ 3.57) and at 229-232 mμ (log ϵ 3.56). (Found: C, 65.09; H, 7.95. $C_{10}H_{14}O_3$ requires C, 65.91; H, 7.73%).

*Methyl 2-Keto-3-methyl*cyclo*hex-$\Delta^{1:6}$-enylacetate* (I: R=Me).—The crude unsaturated keto-acid (m.p. 90-91°, 10 g.) was refluxed with methanol (30 c.c.) and H_2SO_4 (2.5 c.c., *d* 1.84) for 30 hrs. The ester was distilled to furnish a slightly coloured liquid (9 g.), b.p. 125-26°/3 mm, λ_{max} 230 mμ (log ϵ 3.85). (Found: C, 65.45; H, 7.91. $C_{10}H_{14}O_3$ requires C, 65.91; H, 7.73%). The esterification could also be carried out with diazomethane in better yield.

Methyl 2-Keto-3-methyl-6-(diethyl malonate)-cyclo*hexylacetate* (III: R=Me; R_1=H; R_2=CO_2Et; R_3=Et).—The condensation of diethyl malonate (16.8 c.c.) with the preceding unsaturated keto-ester (12.5 g.) in absolute ethanol (5 c.c.) was performed in presence of sodium (0.05 g.) in absolute ethanol (25 c.c.) according to the procedure of Mukherjee (*loc. cit.*). The reaction mixture was allowed to stand at room temperature for 44 hours and after acidification, the product was worked up with ether-benzene mixture. After removal of the solvents, the residue was distilled, b. p. 190-95°/1.5 mm, yield 14.8 g., which was redistilled for analysis, b.p. 185-90°/1.5 mm. The compound is

insoluble in 10% aqueous sodium hydroxide. (Found: C, 60.02; H, 7.66. $C_{17}H_{26}O_7$ requires C, 59.62; H, 7.65%).

Methyl 2-Keto-3-methyl-6-(ethyl cyanoacetate)-cyclohexylacetate (III: R = Me; R_1=H; R_2=CN; R_3=Et).—To a well-cooled solution of sodium ethoxide, prepared from sodium (0.03 g.) and absolute ethanol (10 c.c.), was added dropwise ethyl cyanoacetate (2.7 c.c.) with constant shaking. After 30 minutes, a solution of the unsaturated keto-ester (2.7 g.) in absolute ethanol (4 c.c.) was added dropwise to the enolate with shaking. The reaction mixture was allowed to stand for 44 hrs. The reddish brown reaction mixture was acidified with cold dilute HCl and the precipitated oil was extracted with ether. The ethereal layer was washed with water, dried and distilled to furnish the condensation product (2.1 g), b.p. 180-85°/1 mm. This cyano-ester, in contrast with the malonic ester, is soluble in 10% aqueous NaOH. (Found: C, 61.85; H, 7.62. $C_{15}H_{21}ON_3$ requires C, 61.01; H, 7.14%).

Dimethyl 3-Methylcyclohexan-2-one-1:6-diacetate (III: R=R_3=Me; R_1=R_2=H).—The preceding malonic ester (1.7 g.) was heated to boiling with a mixture of glacial acetic acid (15 c.c.) and HCl (conc., 15 c.c.) in an atmosphere of nitrogen for 16 hrs. The volatile acids were removed under reduced pressure and the brown viscous residue (1.1 g.) furnished only a small amount of a crystalline material, m.p. 143-44°, when the attempt was made to crystallise the acid from acetone-benzene mixture.

The above cyano-ester (0.7 g.) was refluxed with HCl (conc., 10 c.c) for 30 hours and then HCl was removed under reduced pressure. The residue (0.5 g.) furnished a crystalline material, too small for further purification.

The above crude acid (3.2 g.) in ether (50 c.c.) containing a few drops of methanol was esterified with an ethereal solution of diazomethane. The resulting ester was washed with 5%NaOH solution and distilled, b.p. 150-55°/1.5 mm, yield 2.6 g. (Found: C, 60.92; H, 7.97. $C_{13}H_{20}O_5$ requires C, 60.94; H, 7.84%).

Methyl 2-Keto-3-methyl-6-(diethyl methylmalonate) cyclohexylacetate (III: R=R_1=Me; R_2=CO_2Et; R_3=Et).—(*a*). The methylation of the above malonic ester (14.5 g.) in absolute ethanol (15 c.c.) was carried out by following the method of Mukherjee (*loc.cit.*) with sodium (1.2 g) in dry ethanol (40 c c.) and methyl iodide (20 c c.) by heating on a water-bath for 4 hrs. The reaction mixture was decomposed by pouring into ice-water containing a few drops of acetic acid. The precipitated oil was worked up by a mixture of ether and benzene. After removal of the dry solvent, the residue was distilled, b.p. 189-95°/1 mm, yield 9.1 g. (Found: C, 60.24; H, 7.67. $C_{18}H_{28}O_7$ requires C, 60.67; H, 7.91%).

(*b*). To a well-cooled solution of sodium dust (0.11 g.) in dry thiophene-free benzene (5 c.c.) was added a solution of methyl 2-keto-3-methyl-6-(diethyl malonate)-*cyclo*hexylacetate (1.7 g.) in dry thiophene-free benzene (5 c.c.) and the reaction was allowed to proceed at room temperature for 16 hrs. To the resulting dark brown solution was added methyl iodide (2 c.c.) in dry benzene (5 c.c.), and the reaction mixture was refluxed for 4 hrs. The cooled reaction mixture was taken up in ether and the organic solution was washed successively with cold dilute HCl, saturated sodium bicarbonate solution and water. After evaporation of the dry solvent, the residue was

evaporatively distilled at 115-20°/0.4 mm, yield 1.1 g. (Found: C, 60.71; H, 7.80. $C_{18}H_{28}O_7$ requires C, 60.67; H, 7.91%).

Methyl 2-Keto-3-methyl-6-(ethyl methylcyanoacetate)-cyclohexylacetate (III: R=R$_1$=Me; R$_2$=CN; R$_3$=Et).—To a solution of sodium ethoxide, prepared from sodium (0.1 g.) and absolute ethanol (10 c.c), cooled in an ice-bath, was added dropwise a solution of methyl 2-keto-3-methyl-6-(ethyl cyanoacetate)-*cyclo*hexylacetate (1 g.) in ethanol (10 c.c.) with shaking. The reaction mixture was allowed to stand for 30 mins. in the cooling bath when it turned brown. Methyl iodide (2 c.c.) was added and the reaction mixture was immediately heated and refluxed for 4 hrs. Again methyl iodide (1 c.c.) was added and the reaction mixture was refluxed for further 2 hrs. The cooled reaction mixture was diluted with cold water and the precipitated oil was extracted with ether. The ethereal layer was washed with 10% aqueous NaOH solution and water, and dried over anhydrous sodium sulphate. After removal of the solvent, the residue was evaporatively distilled at 140-45°/1.2 mm, yield 0.9 g. (Found: C, 62.48; H, 7.62. $C_{16}H_{23}ON_5$ requires C, 62.10; H, 7.50%).

Methyl 2-Keto-3-methyl-6-(methyl α-propionate)-cyclohexylacetate (III: R=R$_1$=R$_3$=Me; R$_2$=H).—The afore-mentioned methylated malonic ester (2.7 g.) was refluxed with a mixture of glacial acetic acid (20 c.c.) and 20% HCl (20 c.c.) for 18 hours to furnish a gummy acidic material (1.5 g.).

The above methylated cyanoacetic ester (0.8 g.) was refluxed with HCl (conc., 15 c.c.) for 30 hrs. The reaction mixture after cooling was extracted thoroughly with ether to furnish a sticky acidic material (0.45 g.).

The above crude dicarboxylic acid (4.8 g.) in ether (50 c.c.) was esterified with an ethereal solution of diazomethane to afford a colorless ester, b.p. 155-60°/2 mm, yield 3.1 g. (Found: C, 62.78; H, 8.22. $C_{14}H_{22}O_5$ requires C, 62.22; H, 8.17%).

5-Methyl-1 or 3-carbomethoxy-hydrindan-2:4-dione.—To a suspension of sodium methoxide, prepared from sodium dust (0.45 g.) in thiophene-free benzene (10 c.c.) and absolute methanol (0.8 c.c.), was added, in an atmosphere of nitrogen, a solution of dimethyl 3-methyl*cyclo*hexan-2-one-1: 6-diacetate (2.4 g.) in thiophene-free benzene (20 c.c.). The reaction mixture was refluxed for 4½ hours and then cooled and poured into iced HCl (dil.). The benzene layer was separated and the aqueous layer was extracted twice with ether. The combined extract was washed free of acid with water and dried over anhydrous sodium sulphate. After removal of the solvent, the residue was distilled to furnish the desired product (0.9 g.), b.p. 140-45°/1.5 mm, which gave an intense violet colour with alcoholic ferric chloride. (Found: C, 64.34; H, 7.27. $C_{12}H_{16}O_4$ requires C, 64.31; H, 7.18%).

1:5-Dimethyl-3-carbomethoxy-hydrindan-2:4-dione (V).—The cyclisation of the dimethyl ester (III: R=R$_1$=R$_3$=Me; R$_2$=H; 2.6 g.) in dry thiophene-free benzene (20 c.c.) was carried out with sodium dust (0.45 g.) in dry thiophene-free benzene (20 c.c.) and absolute methanol (0.8 c.c.), in an atmosphere of nitrogen, by heating for 5 hours. The brown-red reaction mixture was worked up, as described before, to afford the β-keto ester (0.8 g.), evaporatively distilling at 85-90°/1 mm. It developed a deep violet colour with alcoholic ferric chloride. (Found: C, 65.73; H, 8.21. $C_{13}H_{16}O_4$ requires C, 65.52; H, 7.59%).

5-Methylhydrindan-2 : 4-dione (IV : R=H).—A mixture of the preceding β-keto ester (0.7 g), glacial acetic acid (3 c.c.) and 20% HCl (6 c.c.) was refluxed for 6 hours under nitrogen. The reaction mixture was cooled, diluted with water (40 c.c.) and then extracted thoroughly with ether. The ethereal layer was washed successively with a saturated sodium bicarbonate solution, saturated sodium chloride solution and a small quantity of water. After evaporation of the ether, the residue was evaporatively distilled at 75-78°/1.5 mm, yield 0.35 g. (Found : C, 72.59 ; H, 8.90. $C_{10}H_{14}O_2$ requires C, 72.26 ; H, 8.48%).

The above diketone (0.14 g.) was converted into the semicarbazone (0.2 g.) by the pyridine method. The crude semicarbazone (0.1 g.), m.p. 217-23°, was heated in methanolic solution with 2 : 4-dinitrophenylhydrazine and a few drops of HCl (conc.). The crude red D.N.P. (0.12 g.) was chromatographed to give a red D.N.P. (0.08 g), m.p. 159-60° (decomp.). Two crystallisations from a mixture of absolute ethanol and ethyl acetate (1 : 1) furnished the pure *bis*-2 : 4-dinitrophenylhydrazone, m.p. 164-65° (decomp.). (Found : N, 21.18. $C_{22}H_{22}O_8N_8$ requires N, 21.28%).

1 : 5-Dimethylhydrindan-2 : 4-dione (IV : R=Me).—The ester (V, 0.75 g.) was refluxed with a mixture of glacial acetic acid (10 c.c) and 20% HCl (10 c.c.) in an atmosphere of nitrogen for 10 hours to furnish the desired diketone, evaporatively distilling at 75-80°/1 mm, yield 0.4 g. (Found : C, 73.52 ; H, 8.72. $C_{11}H_{16}O_2$ requires C, 73.30 ; H, 8.93%).

The *bis*-2 : 4-dinitrophenylhydrazone was prepared by following the procedure described before. On crystallisation from a mixture of absolute ethanol and ethyl acetate (1 : 1) it gave two fractions : (*i*) a very small amount of yellow crystals, m.p. 218-20° (decomp.) which could not be purified due to lack of material and (*ii*) more soluble orange crystals, m.p. 180-85° (decomp.). Three crystallisations of the orange material furnished the pure isomer, m.p. 193-94° (decomp.). (Found : N, 20.72. $C_{23}H_{24}O_8N_8$ requires N, 20.72%).

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STUDIES ON THE RELATION BETWEEN CHEMICAL CONSTITUTION AND ULTRAVIOLET ABSORPTION SPECTRA OF OPTICALLY ACTIVE AND RACEMIC COMPOUNDS. PART V. CORRELATION OF ABSORPTION MAXIMA AND 'CHARACTERISTIC' WAVE-LENGTHS OF SOME ALKYL AND ARYL ESTERS OF *d*-CAMPHOR-β-SULPHONIC ACID IN DIFFERENT SOLVENTS

By Bawa Kartar Singh and S. R. G. Sarma

The ultraviolet absorption spectra of methyl, ethyl, phenyl, tolyl (*o*- & *p*-) and naphthyl (α- & β-) esters of *d*-camphor-β-sulphonic acid have been determined in three solvents. The values of λ_{max} have been compared with those of the 'characteristic' wave-lengths (λ_c). There are marked discrepancies in the values of λ_c and λ_{max}. An explanation for these differences is given.

Ultraviolet absorption spectra of methyl, ethyl, phenyl, tolyl (*o*- & *p*-) and naphthyl (α- & β-) esters of *d*-camphor-β-sulphonic acid have been reported in this communication.

Experimental

The compounds mentioned above were prepared and purified according to methods described previously (Singh and Sarma, this *Journal*, 1958, **35**, 49). The absorption measurements were carried out in spectroscopically pure solvents (viz., methanol, ethanol and chloroform) with a Beckman DU ultraviolet spectrophotometer with a view to comparing the 'characteristic' wave-lengths, (λ_c), deduced from Drude's one-term rotatory dispersion equation, with ultraviolet absorption maxima, λ_{max}. The strength of the solutions was 0.50% in the case of methyl and ethyl esters, 0.005% in the case of α- and β-naphthyl esters and 0.10% in the case of *o*- and *p*-tolyl and phenyl esters, except 0.05% in the case of phenyl ester in methyl alcohol. The molecular extinction coefficients (ε) were calculated from the observed values of optical density. The peak values of the molecular extinction coefficients, ϵ_{max}, and the corresponding values of λ_{max} are recorded in Table I.

TABLE I

d-Camphor-β-sulphonates.	Conc. (g./100 c.c.).	Solvent.	$\lambda_{max.}$	$\epsilon_{max.}$	λ_o*.	$\lambda_o - \lambda_{max.}$
1. Methyl	0.50	MeOH	288 mμ	25	320 mμ	32
	,,	EtOH	288	27	314	26
	,,	$CHCl_3$	288	28	320	32
2. Ethyl	0 50	MeOH	288	28	305	17
	,,	EtOH	289	27	332	43
	,,	$CHCl_3$	289	30	292	3
3. Phenyl	0.05	MeOH	260	150	326	66
	0.10	EtOH	260	198	320	60
			285	1 to 2		35
	,,	$CHCl_3$	260	194	307	47
			286	1 to 2		21
4. *o*-Tolyl	,,	MeOH	263	322	316	53
	,,	EtOH	263	347	318	55
	,,	$CHCl_3$	263	340	323	60
5. *p*-Tolyl	,,	MeOH	265	326	312	47
	,,	EtOH	265	333	325	60
	,,	$CHCl_3$	265	383	323	58
6. α-Naphthyl	0.005	MeOH	280	10726	316	36
	,	EtOH	280	10153	340	60
	,,	$CHCl_3$	280	7088	305	25
7. β-Naphthyl	,,	MeOH	275	4847	311	36
	,,	EtOH	275	5654	315	40
	,,	$CHCl_3$	275	3881	317	42

* Singh and Sarma, this *Journal*, 1957, **34**, 787. From Drude's equation.

DISCUSSION

The validity of Drude's rotatory dispersion equation,

$$[\alpha]_\lambda = \Sigma \frac{k}{\lambda^2 - \lambda_o^2},$$

in which k represents the rotation constant and λ_o, the 'characteristic' wave-length of the dominant absorption band governing rotation, has been tested by several workers. Lowry *et al.* (*Phil. Trans.*, 1927, **226A**, 391; *J. Chem. Soc.*, 1924, **125**, 1593) were interested to simply show that the rotatory dispersion equation curve could be represented by a very few terms, whereas Condon (*Rev Mod. Phys*, 1937, **9**, 432) regarded these terms as having average values resulting from the combination of several terms of more fundamental significance. Generally, the rotatory dispersion equation is expressed by one or two terms of Drude's formula, whereas the summation includes several terms of which the first one or two terms may be more important than the succeeding ones, which either are too small or may nearly cancel each other

and are therefore neglected. It is, thus, clear that this mode of representation by *one-* or *two-term* formula is far from reality. The terms found necessary in one- or two-term equation of Drude, within the limits of experimental error, thus, approximately represent the main contribution to the total optical activity. It is for these reasons that λ_o, as determined from Drude's equation, differs from λ_{max}. These differences may be large or small according to circumstances. In the present investigation, the differences between λ_o and λ_{max} lie between 3 mμ for ethyl *d*-camphor-β-sulphonate in chloroform and 66 mμ for phenyl *d*-camphor-β-sulphonate in methyl alcohol. The λ_o, deduced from Drude's *one-term* rotatory dispersion equation,

$$[\alpha]_\lambda = \frac{k}{\lambda^2 - \lambda_o^2},$$

represents the wave-length of the dominant absorption band which governs the rotation. It should therefore be equal to one of the absorption bands (λ_{max}) determined by direct absorption measurements. Again, in deducing λ_o from rotatory dispersion measurements, we employ a very limited and short range of the spectrum from 670.8 mμ to 435.8 mμ, that is, 235 mμ. It is for this reason as well as those mentioned above, that there is discrepancy between the values of λ_o and λ_{max}.

The compounds recorded in Table I may be discussed as follows.

Methyl and Ethyl Esters of d-*Camphor-β-sulphonic Acid.*—The values of λ_{max} for these esters in three solvents are 288 and 289 mμ. They therefore represent the absorption band of the keto group in these compounds. The values of λ_o (Table I) vary from 305 mμ to about 332 mμ except in the case of ethyl ester in chloroform where it is about 292 mμ. The differences (λ_o - λ_{max}) therefore range from 3 to 43 mμ.

Phenyl and Tolyl Esters of d-*Camphor-β-sulphonic Acid.*—In these esters there is a band at λ_{max} 260 to 265 mμ in the three solvents. There is, however, also a second band, λ_{max}, in the case of phenyl ester at 285 mμ in ethyl alcohol and 286 mμ in chloroform. This belongs to the keto group. The value of λ_o varies from about 307 to 326 mμ and thus differs from λ_{max} by 21 to 66 mμ (Table I).

Naphthyl Esters of d-*Camphor-β-sulphonic Acid.*—The value of λ_{max} in the case of α-naphthyl ester is 280 mμ, whereas in that of β-naphthyl ester it is 275 mμ in the three solvents. The ketonic band is associated with about 280 mμ, which is also the absorption maximum (λ_{max}) of naphthyl radical. But the extinction coefficient, ϵ_{max}, of the keto group is much lower than that for the naphthyl radical. This band therefore appears to be due to both these groups. The values of the λ_os, (Table I) vary from 305 to 340 mμ. The difference, λ_o - λ_{max}, ranges between 25 and 60 mμ in the case of these esters.

It may be noted that these seven compounds exhibit rather simple ultraviolet absorption spectra. The alkyl esters exhibit only one band in the three solvents at λ_{max}, 288 to 289 mμ. The phenyl ester exhibits one λ_{max} in three solvents at 260 mμ. It also shows a second band in ethyl alcohol and in chloroform at λ_{max} 285 to 286 mμ. The tolyl esters exhibit only a single band at 260-265 mμ. The naphthyl esters exhibit a band at 275 mμ (α-ester) and at 280 mμ (β-ester).

These values of λ_{max}, thus, are in several cases considerably different from those of λ_o (Table I).

The authors reserve the study of other similar esters of camphor-β-sulphonic acids (*d* and *dl*).

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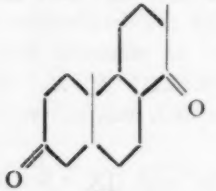
STUDIES IN THE MICHAEL CONDENSATION. PART III. SYNTHESIS OF 1-HYDROXY-2 : 4b-DIMETHYL-7-KETO-1 : 2 : 3 : 4 : 4a : 4b : 5 : 6 : 7 : 9 : 10 : 10a-DODECAHYDRO-PHENANTHRENE

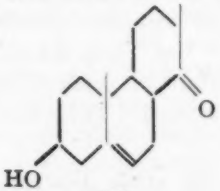
By Amalendu Banerjee and Bidyut Kamal Bhattacharyya

The trimethyl heptane-1 : 3 : 7-tricarboxylate, on the Dieckmann cyclisation, methylation, bromination, dehydrobromination, hydrolysis and decarboxylation furnishes β-(2-keto-3-methyl-*cyclo*hex-$\Delta^{1:6}$-enyl)-propionic acid. The methyl ester of the latter, on the Michael condensation, hydrolysis and esterification, affords methyl β-(2-keto-3-methyl-6-methylacetate-*cyclo*hexyl)-propionate, which on the Dieckmann cyclisation, followed by acid treatment, yields 2-methyldecalin-1 :6-dione. Methyl β-(2-keto-3-methyl-6-ethyl cyanoacetate-*cyclo*hexyl)-propionate, on methylation, followed by the above series of reactions, furnishes 2 :5-dimethyldecalin-1 : 6 dione. The latter, on treatment with ethylyne-glycol, lithium aluminium hydride and acid, furnishes 1-hydroxy-2 :5-dimethyl-decal-6-one, which with the methoiodide of 1-diethylaminobutan-3-one yields 1-hydroxy-2 : 4b-dimethyl-7-keto-1 : 2 : 3 : 4 : 4a : 4b : 5 : 6 : 7 : 9 : 10 : 10a-dodecahydrophenanthrene (III).

In the classical synthesis of cholesterol, Robinson and his collaborators (*J. Chem. Soc.*, 1949, 1855; 1953, 361; 1955, 3348) have utilised Reich's diketone (I) (Reich, *Helv. Chim. Acta*, 1945, **28**, 892) as a relay. During the conversion of the diketone (I) into the Köster-Logemann ketone (II) (*Ber.*, 1940, **73**, 299), Robinson *et al.* (*J. Chem. Soc.*, 1953, 361) have prepared (+) 1-hydroxy-2 :4b-dimethyl-7-keto 1 : 2 : 3 : 4 : 4a : 4b : 5 : 6 : 7 : 9 : 10 : 10a-dodecahydrophenanthrene (III). In an attempt to synthesise Reich's diketone, the synthesis of (III) by the application of the Mannich-Robinson reaction on the hydroxy-ketone (XIV) has been achieved in the following way.



(I)



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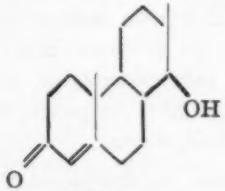


(III)

The conversion of methyl β-(1-carbethoxy-2-keto*cyclo*hexyl)-propionate (Howarth and Mavin, *ibid.*, 1933, 1012) to methyl β-(2-keto-3-methyl-3-carbomethoxy*cyclo*hex-$\Delta^{1:6}$-enyl)-propionate was effected according to the method of Sen Gupta and Bhattacharyya (this *Journal*, 1954, **31**, 337). The above saturated β-keto ester was cleaved with sodium ethoxide and then hydrolysed and esterified to furnish the trimethyl ester (IV), which was cyclised with sodium and methylated *in situ* to afford the substituted β-keto ester (V : R=H). The latter on treatment with bromine gave a crystalline bromo compound (V : R=Br), which on treatment with dimethylaniline furnished the unsaturated compound (VI). The latter on heating with a mixture of acetic and hydrochloric acids gave crystalline β-(2-keto-3-methyl*cyclo*hex-$\Delta^{1:6}$-enyl)-propionic acid. The mother-liquor of the crystalline bromo compound furnished a heavy oil which, on similar treatments, furnished the same crystalline acid (VII : R=H).

The Michael condensation of the ester (VI) with ethyl cyanoacetate yielded the adduct (VIII). The methyl ester of the acid (VII : R = H) was condensed with ethyl cyanoacetate as well as with diethyl malonate, according to the method of Banerjee and Bhattacharyya (this *issue*, p. 457) to afford the condensation products (IX : R = Me ; R_1 = H ; R_2 = CN ; R_3 = Et and R = Me ; R_1 = H ; R_2 = CO_2Et ; R_3 = Et) respectively. Subsequent to the completion of our work (Bhattacharyya and Banerjee, *Science & Culture*, 1957, **23**, 45, 107) Aebli and Grob (*Helv. Chim. Acta*, 1957, **40**, 2185) have reported the synthesis of ethyl β-(2-keto 3-methyl-3-carbethoxy-*cyclo*hex-$\Delta^{1:6}$-enyl)-propionate by a different route. In contrary to our observation, the Swiss authors were unable to hydrolyse this unsaturated ester with either acid or alkali. They have successfully condensed diethyl malonate with this unsaturated compound to produce ethyl β-(2-keto-3-methyl-3-carbethoxy-6-diethyl malonate-*cyclo*hexyl)-propionate in an excellent yield. The latter compound, on treatment with alkali, furnishes the acid (VII : R = H) properties of which agree with those of our preparation.

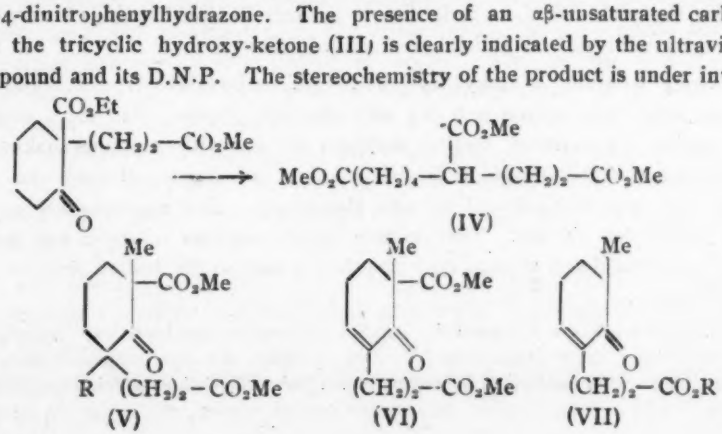
The compound (IX : R = Me ; R_1 = H ; R_2 = CN ; R_3 = Et) was hydrolysed and decarboxylated with acid and then esterified to furnish the dimethyl ester (IX : R = R_3 = Me ; R_1 = R_2 = H) which, on cyclisation with sodium followed by acid treatment, afforded the diketone (XII : R = H). The latter was reduced with lithium aluminium hydride to the crystalline diol (XIII : R = H) which, on dehydration with potassium hydrogen sulphate, followed by dehydrogenation, yielded 2-methylnaphthalene.

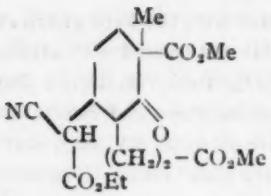
The above cyano-ester (IX : R = Me ; R_1 = H ; R_2 = CN ; R_3 = Et) was methylated according to the procedure of Banerjee and Bhattacharyya (*loc. cit.*) and the resulting product was converted into the dimethyl ester (IX : R = R_1 = R_3 = Me ; R_2 = H) which was cyclised with sodium hydride and then hydrolysed and decarboxylated with acid to yield the diketone (XII : R = Me). This diketone, on reduction with the same reagent, gave presumably a mixture of epimeric diols (XIII : R = Me) from which a pure crystalline component was isolated. The epimeric diols were converted into 2 : 5-dimethylnaphthalene.

It may be mentioned that the crude dicarboxylic acid (IX : R = R_2 = R_3 = H ; R_1 = Me) on pyrolysis with lead carbonate furnished the expected product (XII : R = Me), but the acid (IX : R = R_1 = R_2 = R_3 = H) on similar treatment failed to furnish any ketonic material.

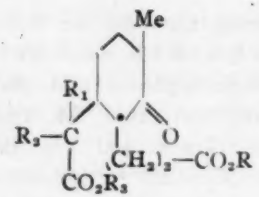
Even, if the Michael addition to an αβ-unsaturated cyclic ketone is axial (Corey, *J. Amer. Chem. Soc.*, 1955, **77**, 1044 ; Johnson, *Chem. & Ind.*, 1956, 167) in cases of simple *cyclo*hexanones having a substituent at C_α, the ring may flip over and then enolise to produce the thermodynamically stable *trans* compounds (e, e) (Bachmann and Fornefeld, *J. Amer. Chem. Soc.*, 1950, **72**, 5529 ; Ginsberg and Pappo, *J. Chem. Soc.*, 1951, 938 ; Corey, *loc. cit.*). The compounds represented by structures (IX) and (VIII), probably, have *trans* configurations. The resulting diketones (XII : R = H and R = Me) from the di-esters (IX : R = R_3 = Me ; R_1 = R_2 = H and R = R_1 = R_3 = Me ; R_2 = H), also have *trans* ring-fusion (Hückel *et al.*, *Annalen* 1925, **441**, 1).

With a view to preparing the diketone (XII: R=Me) with the keto group at C_1 protected, the dimethyl ester (IX: $R=R_1=R_3=Me$; $R_2=H$) was treated with ethyleneglycol in presence of *p*-toluenesulphonic acid (Salmi, *Ber.*, 1938, **71**, 1803 ; Beyler and Sarett, *J. Amer. Chem. Soc.*, 1952, **74**, 1397, ; Lukes, Poos and Sarett, *ibid*, 1952, **74**, 1401 ; Mukherjee, Gandhi and Vig, this *Journal*, 1956, **33**, 853), but unfortunately, the compound (X) could be isolated in a very poor yield. The sodium salt of the crude dicarboxylic acid (IX: $R=R_2=R_3=H$; $R_1=Me$) was treated with sodium borohydride, and the crude hydroxy-dicarboxylic acid was esterified with diazomethane to yield the compound (XI). This hydroxy-ester could be cyclised neither by sodium in benzene nor by sodium ethoxide in ethanol. The observations that 2-methyldecalin-1:6-dione and 2:5-dimethyldecalin-1:6 dione furnished a monosemicarbazone and a mono 2:4-dinitrophenylhydrazone respectively under usual conditions led us to conclude that the keto group at C_1 was more hindered than that at C_6. The semicarbazone of the diketone (XII: R=Me), prepared in the usual way, was reduced with sodium borohydride (cf Taub, Hoffsommer and Wendler, *J. Amer. Chem. Soc.*, 1957, **79**, 452) in ethanol, and the resulting product, when hydrolysed with a solution of oxalic acid, yielded the hydroxy compound (XIV) in extremely poor yield. This hydroxy compound was prepared in a better yield by treating the diketone (XII: R=Me) with ethyleneglycol and *p*-toluenesulphonic acid (cf. Herzog *et al.*, *ibid.*, 1953, **75**, 4425), followed by lithium aluminium hydride and acid. That the hydroxy compound has the structure (XIV), is clearly indicated by its smooth condensation with ethyl formate in presence of sodium methoxide. The crude formylated product was converted into the methylanilinomethylene compound and then subjected to the Mannich-Robinson reaction with methoiodide of 1-diethylaminobutan-3-one in presence of potassium *tert*.-butoxide (Robinson *et al.*, *J. Chem. Soc.*, 1937, 53, ; 1952, 1224 ; 1955, 3341 ; Wilds *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 5794 ; Sarett *et al.*, *ibid.*, 1953, **75**, 422 ; Banerjee, Chatterjee and Bhattacharyya, *ibid.*, 1955, **77**, 408) to yield, after successive treatments with acid and base, 1-hydroxy 2:4b-dimethyl-7-keto-1:2:3:4:4a:4b:5:6:7:9:10:10a-dodecahydrophenanthrene (III) as a pale yellow viscous material in extremely poor yield, characterised through a deep orange crystalline 2:4-dinitrophenylhydrazone. The presence of an αβ-unsaturated carbonyl function in the tricyclic hydroxy-ketone (III) is clearly indicated by the ultraviolet data of the compound and its D.N.P. The stereochemistry of the product is under investigation.





(VIII)



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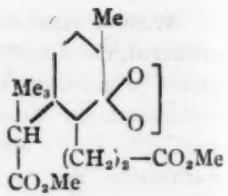
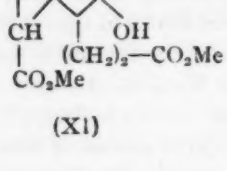


(X)



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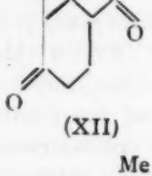

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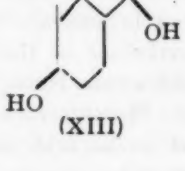

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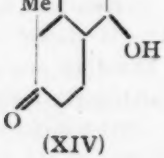

(XIV)

EXPERIMENTAL*

Trimethyl Heptane-1 : 3 : 7-*tricarboxylate* (IV).—Sukh Dev and Rai (this *Journal*, 1957, **34**, 266) described the preparation of ethyl β-(1-carbethoxy-2-keto*cyclo*hexyl)-propionate in ethanolic solution without any experimental detail. It has been observed that the yield of the condensation product is considerably lowered if the reaction temperature is not maintained as described below.

To a cold solution of ethyl *cyclo*hexanone carboxylate (170 g.) and sodium ethoxide, prepared from sodium (0.6 g.) and absolute ethanol (120 c.c.), was added dropwise, during 30 minutes, methyl acrylate (86 g.) with vigorous shaking. The reaction mixture gradually turned yellowish and then brown-red. During the addition the temperature was not allowed to rise above 40°. The reaction was allowed to proceed at 30-35° for 12 hrs. The reddish brown reaction mixture was poured in cold dilute acetic acid and worked up with ether to furnish the desired product (216 g.), b.p. 170-80°/5 mm.

* All m.p.'s. and b.p.'s. are uncorrected. The U.V. absorption spectrum was determined in 95% ethanol by the Unicam spectrophotometer S.P. 500. Analyses of a few compounds were done by Mrs. C. Dutta in the micro-analytical Laboratory of the University College of Science and Technology, Calcutta.

To a hot (55-60°) suspension of sodium ethoxide, prepared from sodium (1.85 g.) and absolute ethanol (23 c.c.), was added the above substituted β-keto ester (104 g.) with shaking, when considerable heat was generated and the reaction mixture turned brown. It was heated on a water-bath for 3½ hrs. The cooled dark brown reaction mixture was poured into iced dilute sulphuric acid and the precipitated oil was worked up with ether and distilled, b.p. 190-95°/5 mm, yield 101 g. The latter was refluxed with 6*N*-HCl (600 c.c.) for 25 hours, when a clear solution was obtained. After removal of the volatile acids, the dried residue was refluxed with a mixture of absolute methanol (225 c.c.) and H_2SO_4 (30 c.c., *d* 1.84) for 35 hours. The cooled reaction mixture was poured into iced water and the precipitated oil was worked up with ether. After removal of the ether, the residue was distilled, b.p. 150-55°/0.8 mm, n_D^{25} 1.4440, yield 72 g. (Found: C, 56.50; H, 8.08. $C_{13}H_{22}O_4$ requires C, 56.90; H, 8.09%).

Methyl β-(2-*Keto*-3-*methyl*-3-*carbomethoxy*-cyclo*hexyl*)-*propionate* (V: R=H).—A mixture of sodium dust (9.2 g.), dry benzene (250 c.c.), the tri-ester (IV, 55 g.) and absolute methanol (0.2 c.c.) was refluxed in an atmosphere of nitrogen for 6 hrs. The dark brown reaction mixture was cooled in an ice-salt bath and then treated with methyl iodide (35 c.c.) with occasional shaking for 1½ hrs. The reaction mixture was allowed to stand at room temperature for 16 hours and after addition of a further quantity of methyl iodide (10 c.c.), it was refluxed for 6 hrs. The cooled reaction mixture was poured into iced water (600 c.c.) containing H_2SO_4 (2 c.c.). The benzene layer was separated and the aqueous layer was extracted twice with ether-benzene mixture. The combined extract was washed with dilute sodium bicarbonate solution and water, and dried over anhydrous sodium sulphate. After removal of the solvent, the residue was distilled, b.p. 135-40°/0.7 mm, yield 35 8 g. (Found: C, 60.61; H, 7.85. $C_{13}H_{20}O_5$ requires C, 60.94; H, 7.84%).

Methyl β-(1-*Bromo*-2-*keto*-3-*methyl*-3-*carbomethoxy*-cyclo*hexyl*)-*propionate* (V: R=Br).—To a solution of the substituted β-keto ester (26 g.) in dry CCl_4 (25 c.c.), cooled to 0-5°, was added dropwise a solution of bromine (6.4 c.c.) in dry CCl_4 (7 c.c.). After the completion of addition, the faint red reaction mixture was allowed to stand for 15 minutes in the cooling bath. The solvent and hydrogen bromide were removed under reduced pressure (water pump) at 60-70°. The residue was treated with petroleum ether (30 c.c., 40-60°) when a heavy oil separated. This was left in the refrigerator for 48 hours when a solid (11.5 g.) separated out, m.p. 65-70°. On concentration of the mother-liquor, a further quantity of the same product (0.5 g.), m.p. 65-70°, was obtained. The compound was crystallised thrice from petroleum ether (40-60°) to furnish colorless crystals, m.p. 78°. (Found: Br, 23.34. $C_{13}H_{19}O_5Br$ requires Br, 23.84%).

The dry heavy oil, obtained from the mother-liquors, responded strongly to the Beilstein test and contained a considerable quantity of the desired bromo compound, as shown below.

Methyl β-(2-*Keto*-3-*methyl*-3-*carbomethoxy*-cyclo*hex*-$\Delta^{1:6}$-*enyl*)-*propionate* (VI).—A mixture of the above crude bromo compound (m.p. 65-70°, 10 g.) and freshly

distilled dimethylaniline (10 c.c.) was heated at 155-65° for 30 mins. The reaction mixture was cooled rapidly and, while still mobile, poured into iced HCl and worked up to furnish the desired product (5.6 g.), b.p. 130-35°/0.4 mm ; n_D^{28} 1.4772 ; λ_{max} 235 mμ (log ε 3.71). (Found : C, 61.09; H, 7.30. $C_{13}H_{18}O_3$ requires C, 61.42 ; H, 7.12%).

A mixture of the above oily bromo compound (16 g.) and dimethylaniline (14 c.c.) was heated and worked up to give the same unsaturated compound (9.5 g.), b.p. 135-40°/0.5 mm, n_D^{28} 1.4775 ; λ_{max} 235 mμ (log ε 3 61). (Found : C, 61.30 ; H, 7.57. $C_{13}H_{18}O_3$ requires C, 61.42 ; H, 7.12%).

The above unsaturated keto-ester was also directly prepared from the semi-solid bromo compound, obtained by bromination, in 70% yield.

β-(2-*Keto*-3-*methyl*-cyclo*hex*-$\Delta^{1:6}$-*enyl*)-*propionic Acid* (VII : R=H).—A mixture of the above unsaturated substituted β-keto ester (3.1 g.), prepared from crystalline bromo compound, glacial acetic acid (6 c.c.) and 6*N*-HCl (6 c.c.), was refluxed for 12 hrs. After dilution with water (100 c.c.), the reaction mixture was extracted with ether. The organic layer was washed with a saturated sodium bicarbonate solution. The alkaline solution was worked up according to the method of Banerjee and Bhattacharyya (*loc. cit.*) to give an acidic material (2 g.) which was crystallised from a mixture of ether and petroleum ether (40-60°), m p. 80-82°, yield 1.6 g. Three crystallisations from the same solvent furnished the pure material, m.p. 88° ; λ_{max} 236 mμ (log ε 3.86). (Found : C, 65.69 ; H, 7.41. $C_{10}H_{14}O_3$ requires C, 65.92 ; H, 7.73%).

The unsaturated substituted β-keto ester (3.5 g.), obtained from the liquid bromo compound, furnished on hydrolysis and decarboxylation an acid (1.8 g.), m.p. 72-75°. On recrystallisation, it furnished the pure marerial, m.p. 87-88°, the mixed m.p. of the latter remained undepressed when mixed with the above keto-acid.

Methyl β-(2-*Keto*-3-*methyl*-cyclo*hex*-$\Delta^{1:6}$-*enyl*)-*propionate* (VII : R=Me).—The above crude acid (51 g., m.p. 75-80°) was refluxed with a mixture of absolute methanol (100 c.c.) and H_2SO_4 (10 c.c., *d* 1.84) for 30 hours to furnish the ester (36 g.), b.p. 115-20°/1 mm ; n_D^{28} 1.4760 ; λ_{max} 232 mμ (log ε 3.77). (Found : C, 67.32 ; H, 8.43. $C_{11}H_{16}O_3$ requires C, 67.33 ; H, 8.2%).

Methyl β-(2-*Keto*-3-*methyl*-6-*diethyl malonate*-cyclo*hexyl*)-*propionate* (IX : R=Me ; R_1=H ; R_2=CO_2Et ; R_3=Et).—The condensation of the above unsaturated keto-ester (4 g.) with diethyl malonate (4.2 g.) in presence of sodium ethoxide, prepared from sodium (0.02 g.) and absolute ethanol (10 c.c.), was allowed to proceed for 7 days according to the method of Banerjee and Bhattacharyya (*loc. cit.*). The reaction mixture furnished the desired product (0.8 g.), b.p. 190-95°/2 mm. (Found : C, 60.25 ; H, 7.62. $C_{18}H_{28}O_7$ requires C, 60.67 ; H, 7.91%).

Methyl β-(2-*Keto*-3-*methyl*-6-*ethyl cyanoacetate*-cyclo*hexyl*)-*propionate* (IX : R=Me ; R_1=H ; R_2=CN ; R_3=Et).—To a stirred solution of sodium ethoxide, prepared from sodium (1.2 g.) and absolute ethanol (150 c.c.), cooled in an ice-salt mixture, was added dropwise ethyl cyanoacetate (8.2 g.). To the enolate after 15 minutes was added dropwise a solution of the unsaturated keto-ester (VI, 78.4 g.) in absolute ethanol (30 c.c.). The reaction mixture was allowed to stand in an ice-salt bath

for 2 hours and then at room temperature for 66 hours. The stirring was continued for 4 hours only. The deep red reaction mixture was worked up to furnish the condensation product (74.1 g.), b.p. 180-90°/1 mm. This cyano-ester is soluble in 10% NaOH solution. (Found : N, 4.53. $C_{16}H_{23}O_5N$ requires N, 4.52%).

The other different conditions for the same condensation are recorded in Table I.

TABLE I

	Unsat. ester.	Ethyl cyanoacetate.	Ethanol.	Sodium.	Time.	% Yield.
1	10.5 g.	14.7 g.	25 c.c.	0.02 g.	60 hrs.	Nil
2	4.0	4.8	22	0.04	48	35-36
3	4.0	5.0	22	0.06	44	46-47
4	19.6	20.5	50	0.20	48	35-36

Methyl β-(2-*Keto*-3-*methyl*-3-*carbomethoxy*-6-*ethyl cyanoacetate*-cyclo*hexyl*)-*propionate* (VIII).—The Michael condensation between the unsaturated keto-ester (VI, 10.1 g.) in absolute alcohol (10 c.c.) with ethyl cyanoacetate (10.5 g.) in presence of sodium ethoxide, prepared from sodium (0.1 g.) and absolute ethanol (30 c.c.), was performed, as described before, by allowing the reaction to proceed for 66 hrs. The reddish brown reaction mixture was worked up to furnish a thick yellow oil (7.8 g.), b.p. 210-15°/0.4 mm. This condensation product is soluble in 10% NaOH solution. (Found : C, 58.75 ; H, 6.91. $C_{18}H_{25}O_7N$ requires C, 58 85 ; H, 6.85%).

Methyl β-(2-*Keto*-3-*methyl*-6-*ethyl methylcyanoacetate*-cyclo*hexyl*)-*propionate* (IX : R=R_1=Me ; R_2=CN ; R_3=Et).—The methylation of the above cyano-ester (15.5 g.) in absolute alcohol (10 c.c.) was performed with sodium ethoxide, prepared from sodium (1.2 g.) and absolute ethanol (35 c.c.), and methyl iodide (14 c.c.) by refluxing for 5 hours (Banerjee and Bhattacharyya, *loc. cit.*). The reaction mixture was worked up with ether and cold 10% NaOH solution to give the desired product (10.3 g.), b.p. 185-90°/1 mm. (Found : N, 4.07. $C_{17}H_{25}O_5N$ requires N, 4.33%).

Methyl β-(2-*Keto*-3-*methyl*-6-*methyl acetate*-cyclo*hexyl*)-*propionate* (IX : R=R_3=Me ; R_1=R_2=H).—The cyano compound (IX : R=Me ; R_1=H ; R_2=CN ; R_3=Et ; 12.8 g.) was refluxed with HCl (conc., 120 c.c.) for 40 hours. The reaction mixture was worked up as described before. The glassy acidic material (8.6 g.) was esterified with an ethereal solution of diazomethane. The ester was worked up with ether and 5% NaOH solution to furnish the dimethyl keto-ester (6.9 g.), b.p. 155-60°/1 mm ; $n_D^{31°}$ 1.4695. (Found : C, 61.92 ; H, 8.07. $C_{14}H_{22}O_5$ requires C, 62.19 ; H, 8.21%).

Methyl β-(2-*Keto*-3-*methyl*-6-*methyl* α-*propionate*-cyclo*hexyl*)-*propionate* (IX : R=R_1=R_3=Me ; R_2=H).—The cyano-ester (IX : R=R_1=Me ; R_2=CN ; R_3=Et ; 7.5 g.) was refluxed with HCl (conc., 75 c.c.) for 40 hrs. The acidic material (4.5 g.), thus obtained, was refluxed with a mixture of absolute methanol (25 c.c.) and H_2SO_4 (3.5 c.c., *d* 1.84) for 30 hours to furnish the ester (4.1 g.), b.p. 160 65°/1 mm ; n_D^{31} 1.4660. (Found : C, 63.14 ; H, 8.60. $C_{15}H_{24}O_5$ requires C, 63.39 ; H, 8.51%).

2-*Methyldecalin*-1 : 6-*dione* (XII : R=H).—A mixture of sodium dust (0.8 g.), dry thiophene-free benzene (30 c.c.), the ester (IX : R=R_3=Me ; R_1=R_2=H ; 5.8 g.)

and two drops of methanol was refluxed in an atmosphere of nitrogen for 4 hrs. The reddish brown reaction mixture was decomposed with iced HCl and worked up to furnish the crude β-keto ester (5.2 g.) which gave an intense violet coloration with alcoholic ferric chloride solution. The above β-keto ester was refluxed with a mixture of glacial acetic acid (15 c.c.) and 6*N*-HCl (20 c.c.) in an atmosphere of nitrogen for 12 hrs. After dilution with water (50 c.c.), the reaction mixture was worked up with ether and sodium bicarbonate solution. After removal of the ether, the residue was distilled to give the diketone (1.3 g.), b.p. 115-20°/4 mm, which solidified on standing, m.p. 66-69°. Two crystallisations from petroleum ether furnished the pure material, m.p. 79°. (Found: C, 72.90; H, 8.95. $C_{11}H_{16}O_2$ requires C, 73.30; H, 8.91%).

The diketone (0.15 g.) was converted into the mono-semicarbazone (0.2 g.), m.p. 205-208° (decomp.), by the pyridine method. Three crystallisations from methanol gave the pure material, m.p. 211° (decomp.). (Found: N, 17.61. $C_{12}H_{19}O_2N_3$ requires N, 17.70%).

To the boiling suspension of the semicarbazone (0.12 g.), 2:4-dinitrophenylhydrazine (0.2 g.) and methanol (10 c.c.) were added 5–6 drops of HCl (conc.) when a clear red solution was obtained. On concentration, a yellowish red precipitate (0.25 g.), m.p. 204-210° (decomp.), was obtained. It was chromatographed over alumina using benzene as the eluting solvent. Three crystallisations of the product (0.2 g.) from a mixture of 95% ethanol and ethyl acetate (1:1) furnished yellow crystals of *bis*-2:4-dinitrophenylhydrazone, m.p. 220° (decomp.). (Found: N, 20.92. $C_{23}H_{24}O_8N_8$ requires N, 20.72%).

2:5-*Dimethyldecalin*-1:6-*dione* (XII: R=Me).—(*a*). A mixture of the keto-dimethyl ester (IX: $R=R_1=R_3=Me$; $R_2=H$; 2.8 g.), dry thiophene-free benzene (25 c.c.), two drops of absolute methanol and powdered sodium hydride (0.5 g.) was refluxed in an atmosphere of nitrogen until the evolution of hydrogen had ceased (usually 3 hrs.). The red reaction mixture was decomposed with iced dilute HCl and worked up to furnish a material (2.5 g.) which gave a violet colour with alcoholic ferric chloride solution. The β-keto ester was refluxed with 6*N*-HCl (40 c.c.) for 12 hours. The reaction product was worked up with ether and bicarbonate solution to give the desired diketone (1.2 g.), b.p. 120-25°/3 mm. The latter was evaporatively distilled at 80-85°/0.4 mm; n_D^{30} 1.4940; λ_{max} 305mμ (log ε 2.56). (Found: C, 73.87; H, 9.42. $C_{12}H_{18}O_2$ requires C, 74.22; H, 9.32%).

When a smaller quantity of sodium hydride (0.35 g.) was used in the above experiment, the yield of the desired diketone was 58%.

(*b*). To a supension of sodium methoxide, prepared from sodium dust (0.8 g.) and absolute methanol (1.4 c.c.) under thiophene-free benzene (25 c.c.), was added a solution of the above keto-dimethyl ester (5.8 g.) in dry thiophene-free benzene (5 c.c.). The reaction mixture was refluxed in an atmosphere of nitrogen for 6 hrs. The reddish brown reaction mixture was worked up and heated with 6*N*-HCl (50 c.c.) to furnish the diketone (1.4 g.).

(*c*). A mixture of the keto-diester (5.6 g.), dry thiophene-free benzene (30 c.c.), sodium dust (0.8 g.) and two drops of absolute methanol was refluxed in an atmosphere of nitrogen for 3 hrs. The dark brown reaction mixture, after working up, furnished the crude β-keto ester (5 g.) which was refluxed with 2.7*N*-NaOH solution (22.5 c.c.) for 3 hrs. On working up, it gave the diketone (1.15 g.).

(*d*). An intimate mixture of the crude dicarboxylic acid (IX : $R=R_2=R_3=H$; $R_1=Me$; 4.5 g.) and freshly prepared dry lead carbonate (22.5 g.) was heated under nitrogen at 270-80° for 1 hour under reduced pressure (water aspirator). The temperature was then increased to 300° and the reaction was allowed to proceed for further 30 mins. The brown oily distillate was taken up in ether. The ethereal solution was washed with dilute sodium bicarbonate solution and water, and dried. After removal of the solvent, the residue was distilled, b.p. 120-25°/3 mm, yield 1.5 g., n_D^{28} 1.4970. (Found : C, 73.98 ; H, 9.19. $C_{12}H_{18}O_2$ requires C, 74.22 ; H, 9.32%).

The above diketone (0.2 g.) was converted into the semicarbazone (0.35 g.), m.p. 218-20° (decomp.), by the pyridine method. Two crystallisations from methanol furnished the mono-semicarbazone, m.p. 226-27°, containing probably a little *bis*-semicarbazone. (Found : N, 17.52. $C_{13}H_{21}O_2N_3$ requires N, 16.71%).

The crude semicarbazone (0.25 g.) was converted into the red 2 : 4-dinitrophenylhydrazone (0.5 g.) by the method described before. It was purified by chromatography and then crystallised thrice from a mixture of 95% ethanol and ethyl acetate (1 : 1) to yield orange-red *bis*-2 : 4-dinitrophenylhydrazone (0.3 g.), m.p. 224-25° (decomp.). (Found : N, 20.16. $C_{24}H_{26}O_8N_8$ requires N, 20.20%).

To a clear solution of 2 : 4-dinitrophenylhydrazine (0.4 g.) in acetone-free methanol (5 c.c.) and a few drops of HCl (conc.) was added a solution of the above diketone (0.2 g.) in acetone-free methanol (2 c.c.). The reaction mixture was boiled for 10 minutes when a yellowish red precipitate was obtained. The crude D.N.P. (0.35 g.) was chromatographed and crystallised twice from a mixture of ethanol and ethyl acetate (1 : 1) to furnish yellow flakes of mono-2 : 4-dinitrophenylhydrazone (0.2 g.), m.p. 210-12° (decomp.). The mixed m.p. of mono- and *bis*-2 : 4 dinitrophenylhydrazones was 203-204° (decomp.). (Found : N, 14.83. $C_{18}H_{22}O_5N_4$ requires N, 14.96%).

2-*Methyldecalin*-1 : 6-*diol* (XIII : R=H).—To a suspension of lithium aluminium hydride (0.6 g.) in dry ether (30 c.c.) was added dropwise with shaking a solution of the 2-methyldecalin-1 : 6-dione (0.75 g.) in dry ether (10 c.c.), when a white precipitate was formed. A further quantity of dry ether (10 c.c.) was added and the reaction was allowed to proceed at room temperature for 48 hrs. The reaction mixture was decomposed with water, followed by 10% H_2SO_4 solution (50 c.c.). The ethereal layer was separated and the aqueous layer was extracted with ether. The combined extract was washed with a small quantity of water and dried over anhydrous sodium sulphate. After removal of ether, the solid residue (0.75 g.), m.p. 172-75°, was crystallised twice from a mixture of ether and ethanol (1 : 1) to yield the pure diol, m.p. 179-80°. (Found : C, 71.71 ; H, 11.01. $C_{11}H_{20}O_2$ requires C, 71.71 ; H, 10.91%).

2 : 5-*Dimethyldecalin*-1 : 6-*diol* (XIII : R=Me).—The compound (XII : R=Me ; 0.95 g.) was reduced with lithium aluminium hydride (1 g.) in ether (75 c.c.). It

was worked up to furnish the semi-solid diol (0 85 g.) which was crystallised from a mixture of ethanol and ether to give the diol (0.4 g.), m.p. 144-45°. On recrystallisation from the same solvent-mixture it furnished needle-shaped crystals, m.p. 144-45°. (Found: C, 72.52; H, 10.80. $C_{12}H_{22}O_2$ requires C, 72.71; H, 11.1₹%). The mother-liquor on concentration furnished a thick oil (0.45 g.).

2-*Methylnaphthalene*.—An intimate mixture of the diol (XIII: R=H; 0.6 g.) and fused powdered potassium hydrogen sulphate (3 g.) was introduced in a preheated chamber, maintained at 180°, and left there for 1 hour when an oily distillate collected. The reaction tube was evacuated (water pump) and the temperature raised to 200°. The oil (0.35 g.), thus obtained, was heated with a mixture of selenium (2 g.) and sulphur (0.25 g.) at 210 15° for 16 hours and then at 250-60° for 16 hours and finally at 280° for 2 hrs. The reaction mixture was worked up with benzene. After evaporation of the solvent, the residue was evaporatively distilled at 150-60°/40 mm. The solid distillate (0.11 g.), m.p. 31-32°, did not depress the m.p. of an authentic sample of 2-methylnaphthalene. The 2-methylnaphthalene was converted in to the picrate, m.p. 114-15° which, when admixed with an authentic sample, did not depress the m.p.

1:6-*Dimethylnaphthalene*.—The above semi-solid diol (XIII: R=Me; 0.7 g.) was dehydrated with fused potassium hydrogen sulphate (3.5 g.), as described before, to furnish the unsaturated compound (0.45 g.) which was heated with a mixture of selenium (2.5 g.) and sulphur (0.3 g), as described before. The reaction mixture was worked up to give an oily product (0.175 g.) which was converted into the picrate. On crystallisation from ethanol, it furnished the pure product, m.p. 113° (Weissgerber and Krüber, *Ber.*, 1919, **52**, 349, record m.p. 114°). (Found: N, 10.69. Calc. for $C_{18}H_{15}O_7N_3$: N, 10.90%).

1-*Hydroxy*-2:5-*dimethyl-decal*-6-*one* (XIV).—(*a*). A mixture of the diketone (XII: R=Me; 2 g.), dry thiophene-free benzene (100 c.c.), freshly distilled ethyleneglycol (0.6 c.c.) and *p*-toluenesulphonic acid (0.03 g.) was refluxed, using a Dean and Stark constant water separator and utilising a lump of fused calcium chloride to absorb the water separated. To the reaction mixture was added a further quantity of *p*-toluenesulphonic acid (0.01 g.) and the refluxing was continued for 1 hour more. The cooled reaction mixture was poured into saturated sodium carbonate solution. After separation of the benzene layer, the aqueous layer was extracted twice with benzene. The combined extract was washed twice with water and dried over anhydrous sodium sulphate. After removal of the solvent, the residue (2.4 g.) in dry ether (30 c.c.) was added to a suspension of lithium aluminium hydride (1.5 g.) in dry ether (30 c.c.) with shaking. The occasional shaking was continued for 2 hours and the reaction was allowed to proceed at room temperature for 48 hrs. The reaction mixture was worked up as before and the residue (2.2 g.), thus obtained, was refluxed with a mixture of methanol (20 c.c.) and 1*N*-H_2SO_4 (10 c.c.) for 75 mins. After removal of most of the methanol on a steam-bath under reduced pressure (water pump), the residual liquid was diluted with water (50 c.c.) and the precipitated oil was thoroughly extracted with ether. The ethereal layer was washed with water and dried over anhydrous sodium sulphate. After removal of the solvent, the oily residue (1.9 g.), λ_{max} 302 mμ

(log ε 2.43), was chromatographed over alumina (85 g.). The fractions eluted with petroleum ether (60-80°) were combined and evaporatively distilled at 80-85°/0.4 mm to give the diketone (0.4 g.), identified through its D.N.P. The fractions, eluted with a mixture of petroleum ether (60-80°) and benzene (1 : 1), were combined and evaporatively distilled at 95-98°/0.2 mm to give the hydroxy-ketone (1.4 g.), which was again evaporatively distilled at 105-10°/0.4 mm to furnish a heavy colorless oil, n_D^{34} 1.4968. (Found : C, 73.03 ; H, 10.28. $C_{13}H_{20}O_2$ requires C, 73.45 ; H, 10.24%).

The 2 : 4-dinitrophenylhydrazone (0.15 g., m.p. 219-21° decomp.) was prepared from the above hydroxy-ketone (0.1 g.) and purified through chromatography. Two crystallisations from a mixture of ethanol and benzene (1 : 1) furnished long yellow needles, m.p. 223-24° (decomp.). The mixed m.p. of the latter with the D.N.P. of the diketone (XII : R = Me) was 202-205° (decomp.). (Found : N, 14.21. $C_{18}H_{24}O_5N_4$ requires N, 14.88%).

(*b*). To a solution of the semicarbazone of 2 : 5-dimethyldecalin-1 : 6-dione (m.p. 226-27°, 0.2 g.) in 50 c.c. of absolute ethanol, cooled in ice, was added finely powdered sodium borohydride (0.75 g.). The reaction mixture was shaken occasionally for 30 minutes when the sodium borohydride went into solution. Again, a further quantity of sodium borohydride (0.25 g.) was added and the reaction was allowed to proceed for 24 hours at room temperature. The reaction mixture was neutralised with 10% acetic acid and the volatile solvents were removed under reduced pressure (water pump). The residual material (0.25 g.), which could not be crystallised, was refluxed with 5% aqueous oxalic acid (40 c.c.) for 12 hrs. The cooled reaction mixture was extracted with ether. The ethereal layer was washed with a saturated sodium bicarbonate solution and water, and dried. After removal of ether, the residue (0.06 g.) was evaporatively distilled at 105-10°/0.4 mm to furnish the hydroxy ketone (0.04 g.). The latter was converted into the 2 : 4-dinitrophenylhydrazone, m.p. 223-24° (decomp.). (Found : N, 15.32. $C_{18}H_{24}O_5N_4$ requires N, 14.88%). The mixed m.p. of this D.N.P. and the D.N.P. of the aforementioned preparation was undepressed. The D.N.P. of the hydroxy-ketone was less soluble in benzene and more in ethanol compared to the D.N.P. of the diketone (XII : R = Me). Reduction of the above semicarbazone in tetrahydrofuran did not give any useful product.

1-*Hydroxy*-2 : 4b-*dimethyl*-7-*keto*-1 : 2 : 3 : 4 : 4a : 4b : 5 : 6 : 7 : 9 : 10 : 10a-*dodecahydrophenanthrene* (III).—To an ice-cold suspension of sodium methoxide, prepared from sodium dust (0.4 g.) and absolute methanol (0.7 c.c.), in dry thiophene-free benzene (10 c.c.) was added, in an atmosphere of nitrogen, a solution of the above hydroxy-ketone (XIV, 1.6 g.) and ethyl formate (1.6 c.c.) in dry thiophene-free benzene (5 c.c.) with shaking. The reaction mixture was shaken for 2 hours in the cold and then left at room temperature for 48 hours, when a brown viscous semi-solid mass precipitated out. To the reaction mixture iced water (25 c.c.) was added and the benzene layer was separated. The organic layer was washed twice with cold 2% NaOH solution. The combined alkaline solutions were cooled in ice and acidified with iced HCl. (dil.) The precipitated oil was extracted thoroughly with ether. The ethereal layer was washed with water and saturated common salt solution and filtered through

anhydrous sodium sulphate. After removal of the solvent, the residue (1.8 g.), which gave an intense violet colour with alcoholic ferric chloride solution, was dissolved in dry thiophene-free benzene (75 c.c.) and then treated with freshly distilled monomethylaniline (1 8 c.c.). The benzene was slowly distilled from a boiling water-bath in the course of 1 hour. A fresh quantity of thiophene-free benzene (75 c.c.) was again added and the benzene was removed, as described before. This procedure was repeated for 5 hours and then the benzene was completely removed from the reaction mixture under reduced pressure (water pump). The yellowish brown residue was kept at 70-80°/4 mm for 30 mins. The dry viscous brown oily methylanilinomethylene compound (2.6 g.), which did not crystallise, decomposed when attempt was made to evaporatively distil it and did not give any positive ferric reaction.

To a stirred mixture of the methoiodide, prepared from 1-diethylaminobutan-3-one (1.5 g.) and methyl iodide (1.5 c.c.), and a solution of the aforementioned crude methylanilinomethylene compound (2.6 g.) in a mixture of dry thiophene-free benzene (5 c.c.) and *tert.*-butanol (10 c.c.), cooled in an ice-bath, was added dropwise in an atmosphere of nitrogen a solution of potassium *tert.*-butoxide, prepared from potassium metal (0.6 g.) and *tert.*-butanol (15 c.c.). A further quantity of *tert.*-butanol (5 c.c.) was used to wash down the adhering butoxide. After completion of the addition, the stirring of the cooled reaction mixture was continued for 3 hours. The reaction was allowed to proceed at room temperature for 16 hrs. After refluxing the reaction mixture for 2 hours, the solvents were removed under reduced pressure (water pump) and the dark coloured residue was acidified with a solution of glacial acetic acid (3 c c.) in water (100 c.c.). The resulting oily suspension was extracted thoroughly with a mixture of ether and benzene. The organic layer was washed with water and dried over anhydrous sodium sulphate. After removal of the solvent, the residue (3.1 g.) was refluxed with 10% HCl solution (100 c.c.) in an atmosphere of nitrogen for 2 hrs. The cooled, dark brown reaction product was extracted with a mixture of ether and benzene. The organic layer was washed with water and dried. After evaporation of the solvent, the residue (2.1 g.) was refluxed with 8% KOH solution (50 c.c.) for 3 hrs. The resulting tarry suspension was cooled in ice and then acidified with HCl (cold, dil.) and extracted with the same solvent mixture. The organic layer was washed with water, dilute sodium bicarbonate solution and water, and dried. After evaporation of the solvent, the tarry residue (.8 g.) was fractionated by evaporative distillation under 0.2 mm : (*i*) 90-100° (0.5 g.), probably the hydroxy ketone ; (*ii*) 125-30° (0.3 g.), viscous opaque glassy material ; (*iii*) 150-60° (traces). Fraction (*ii*) was again evaporatively distilled to yield a low-boiling product, 90-95°/0.2 mm (0.05 g.) and the desired material (0.25 g.), b.p. 125°/0.2 mm, λ_{max} 241 mμ (log ε 4.09). The latter was again evaporatively distilled very slowly for analysis ; b.p. 130-35°/0.4 mm ; λ_{max} 241 mμ (log ε 4.07). (Found : C, 77.50 ; H, 9.97. $C_{16}H_{24}O_2$ requires C, 77.36 ; H, 9.74%).

The above alkaline treatment with 10, 15 and 20% aqueous NaOH did not improve the yield of the desired αβ-unsaturated ketone.

To a solution of the above tricyclic ketone (0.06 g.) in methanol (1 c.c.) was added a solution of 2 : 4-dinitrophenylhydrazine (0.05 g.) in methanol (2 c.c.) contain-

ing one drop of HCl (conc.). The reaction mixture was boiled for 5 minutes when an orange-red precipitate was formed. The crude product (0.06 g.), m.p. 226-30° (decomp.) was chromatographed on alumina, using benzene. The crude solid, thus obtained, was crystallised four times from a mixture of methanol and ethyl acetate (1:1) to give deep orange crystals (0.014 g.), m.p. 243-44° (decomp.), λ_{max} 383 mμ (log ε 4.37). (Found: C, 61.55; H, 6.69; N, 13.19. $C_{22}H_{28}O_5N_4$ requires C, 61.67; H, 6.58; N, 13.07%).

Methyl β-(2-*Ethylenedioxy*-3-*methyl* 6-*methyl* α-*propionate*-cyclo*hexyl*)-*propionate* (X).—A mixture of the keto-diester (IX: $R=R_1=R_3=Me$; $R_2=H$; 9.5 g.), dry thiophene-free benzene (60 c.c.), freshly distilled ethyleneglycol (2.2 g.) and *p*-toluenesulphonic acid (0.04 g.) was refluxed, using a Dean and Stark water separator, for 6 hrs. Another lot of *p*-toluenesulphonic acid (0.02 g.) was added and the reaction mixture was refluxed for a further period of 1½ hrs. The reaction mixture was worked up, as described before, to give a heavy oil (9 5 g.) which was distilled, b.p. 150-55°/0.3 mm. This material (8 5 g.), on repeated fractional and evaporative distillations, furnished a colorless oil (0.5 g.), evaporatively distilling at 115-20°/0.3 mm; n_D^{34} 1.4734. (Found: C, 61 94; H, 8.82. $C_{17}H_{28}O_6$ requires C, 62.19; H, 8.58%).

On cyclisation of the bulk material with either sodium dust or sodium hydride in benzene, followed by working up of the reaction product with a saturated solution of sodium dihydrogen phosphate and hydrolysis with alkali, furnished a mixture of the diketone and 1-ethylenedioxy-2: 5-dimethyldecal-6-one, evaporatively distilling at 110°/3 mm. (Found: C, 72.04, 72.73; H, 9.14, 9.40%). The latter was converted into the mono-2:4-dinitrophenylhydrazone in acid solution, m.p. 210-12° (decomp.).

Methyl β-(2-*Hydroxy*-3-*methyl*-6-*methyl* α-*propionate*-cyclo*hexyl*)-*propionate* (XI). —A mixture of the above ester (IX: $R=R_1=R_3=Me$; $R_2=H$; 2.28 g.), methanol (10 c.c.) and a solution of NaOH (1.28 g.) in water (2 c.c.) was refluxed in an atmosphere of nitrogen for 3 hrs. The methanol was removed and the residue after dilution with water was extracted with ether. The alkaline solution was acidified with 6*N*-HCl and the precipitated oil was worked up. To a cooled solution of the acidic material (2 g.), thus obtained, dissolved in 2.71*N*-NaOH solution (3 c.c.) and water (18 c.c.), was added sodium borohydride (1 g.) and the reaction was allowed to proceed at room temperature for 16 hrs. The reaction mixture, after refluxing, in an atmosphere of nitrogen for 1 hour, was poured into iced HCl. The precipitated oil was worked up and the acidic material, thus obtained, was esterified with diazomethane in ethereal solution to furnish the ester (0.7 g.), evaporatively distilling at 115-20°/0.2 mm. (Found: C, 63.25; H, 9.25. $C_{15}H_{26}O_5$ requires C, 62.90; H, 9.15%).

The cyclisation of the afore-mentioned hydroxy-ester either with sodium methoxide in benzene or with sodium methoxide or ethoxide in absolute alcohol, furnished the unchanged ester as the major component.

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CHEMICAL EXAMINATION OF THE SEEDS OF *LUFFA ACUTANGULA* ROXB.

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A crystalline bitter principle, cucurbitacin B and an acid sap. genin, oleanolic acid, have been isolated and identified from the seeds of *Luffa acutangula* Roxb.

Luffa acutangula Roxb. (Family *Cucurbitaceae*, commonly known as *Jhinga* in Bengali) is cultivated as a vegetable throughout India. Martin de la Torre and Santos (*Rev. filipina med. farm.*, 1939, **30**, 169; *Chem. Abst.*, 1939, **33**, 5593) isolated a bitter substance, $C_{15}H_{24}O_4$, m.p. 182-84°, from *Luffa cylindrica* (Linn.) Roem. Rangaswami and Sambamurthy (*Indian J. Pharm.*, 1954, **16**, 225) also reported the isolation of a bitter principle, m.p. 182-84°, from the seeds of *L. cylindrica* Roem., known in Bengal as *dhundul*. Choudhury, Sharma and Siddiqui (*J. Sci. Ind. Res.*, 1951, **10B**, 26) obtained a bitter principle, designated as 'amarin', $C_{19}H_{26}O_5$, m.p. 182°, $[\alpha]_D^{28}$ + 88° (ethanol), from the seeds of *L. acutangula* Roxb., var. *amara* Clarke. We have examined the seeds of *L. acutangula* Roxb. and the report of our preliminary investigation is mentioned herein.

From the ether extract of the defatted seeds was isolated in good yield (0.67%) a highly crystalline, colorless, bitter substance, which on chromatographic resolution on a column of cellulose powder, impregnated with formamide, gave a colorless crystalline compound, m.p. 175-82°, as the major product. A slightly higher melting fraction was also obtained during chromatography, but due to poor yield further work could not be carried out. The fraction (m.p. 175-82°) on repeated crystallisation from aqueous methanol and ethanol gave a constant melting compound, $C_{32}H_{48}O_8$, m.p. 182-85°, $[\alpha]_D$ +87.4° (96% ethanol).

From the alcoholic extract of the seeds a crude saponin in low yield was also isolated, which on hydrolysis gave an acid sapogenin, $C_{30}H_{48}O_3$, m.p. 304-308°, $[\alpha]_D^{24}$ + 78.3° (chloroform). Barua and Bose (*Trans. Bose Res. Inst*, 1956-57, **21**, 19; Barua, *Science & Culture*, 1957, **23**, 154) also isolated the same acid from the seeds of *L. cylindrica*. The monomethyl ester of the acid, $C_{31}H_{50}O_3$, m.p. 198-200°, furnished a monoacetate, $C_{33}H_{52}O_4$, m.p. 222°, $[\alpha]_D^{24}$ + 70.4° (chloroform). The acid sapogenin was identified as oleanolic acid by the determination of mixed m.p. of the methyl ester of the compound with an authentic sample of methyl oleanolate.

Recently Enslin *et al.* (*J. Sci. Fd. Agric.*, 1954, **9**, 410; 1956, **7**, 646 et seq) reported the isolation of a bitter principle, cucurbitacin B, $C_{32}H_{40-42}O_7$, m.p. 180-82°, $[\alpha]_D^{28}$ + 87.5° (ethanol), from several plants of the *Cucurbitaceae* family and subsequently reported (*South African Ind. Chem.*, April, 1957) a higher melting point, 184-86° and $[\alpha]_D$ + 88° (96% ethanol) for cucurbitacin B. Rivett and Herbstein

(*Chem. & Ind.*, 1957, 393) suggested the molecular formula of the above compound to be $C_{32}H_{48}O_8$ on the basis of molecular weight determination by the X-ray method. The physical and chemical properties of the compound, isolated by the present authors (m.p. 182-85°), agreed closely with those of cucurbitacin B and their identity was established by mixed m.p. with an authentic sample of cucurbitacin B and also by paper chromatography. It appears that cucurbitacin B is identical with 'amarin', reported by the Indian and Philippine workers (*loc. cit.*) from *Luffa* species. From a private communication from Dr. P. R. Enslin, we came to learn that a crude extract obtained by them from the seeds of *L. acutangula* gave a strong spot for cucurbitacin B on paper chromatogram.

*EXPERIMENTAL

Isolation of Cucurbitacin B.—Air-dried, powdered seeds (2 kg.) were defatted with petroleum ether (b.p. 60-80°) and then extracted with ether in a Soxhlet apparatus for 30 hours. The ether extract was concentrated to a small volume (100 c.c.) and left overnight when a crystalline mass separated. On filtration and washing with a small quantity of ether, colorless crystals, m.p. 170-75°, were obtained. A second crop of crystals was obtained on further concentrating the mother-liquor and diluting with petroleum ether (b p. 60-80°), total yield 13.4 g.

The above material (1 g.) was dissolved in benzene (15 c.c.) and was adsorbed on a column (28 cm × 2 cm) of formamide-impregnated cellulose powder (25% formamide in ethanol). The column was eluted with 300 c.c. of petroleum ether (b.p. 40-60°) and the residue left on evaporation of the solvent melted at 175-82°. The column was then eluted with 250 c.c. of petroleum ether (b.p. 40-60°)–benzene mixture (3 : 1), which gave a further amount of the above substance. On elution with the same solvent mixture (1 : 1, 300 c.c. and 1 : 3, 200 c.c.) a fraction, m.p. 190-200°, in very poor yield, was obtained. The residue from the petroleum ether fraction was repeatedly crystallised from aqueous ethanol and methanol to give a constant melting crystalline compound, m.p. 182-85°. This was found to be bitter and it responded to the Liebermann-Burchardt test. The m.p. of this compound was not depressed when admixed with an authentic sample of cucurbitacin B. (Found : C, 68.98 ; H, 8.73. Calc. for $C_{32}H_{48}O_8$: C, 68.54 ; H, 8.63%).

The crude bitter principle was also subjected to fractional crystallisations from aqueous ethanol when the fractions : (1) m.p. 180-85°, (2) m.p. 190-98° and (3) m.p. 207-22° were obtained. The last two fractions were obtained in extremely poor yield and therefore could not be further studied.

Paper Chromatography of the Bitter Principle.—The bitter principle was subjected to paper chromatography by following the technique of Enslin *et al.* (*J. South African Chem. Inst.*, 1954, 7, 131) to study the homogeneity and also for comparison with an authentic sample of cucurbitacin B. In our experiments, we used Whatman No. 1 filter paper, impregnated with 25% formamide in ethanol, and adopted the ascending method of development. The spots were conveniently located by their

* The m.p.'s are uncorrected. The microanalyses of the samples were carried out by Mrs. C. Dutta.

quenching in the ultraviolet light and also by spraying with 0.5% solution of $KMnO_4$ in saturated copper acetate. Our compound was co-chromatographed with the authentic sample of cucurbitacin B. The crude material also gave only one strong spot for cucurbitacin B. The R_f values of our compound in chloroform at 29° and in benzene at 28° are 0.91 and 0.63 respectively and those of the authentic sample of cucurbitacin B are 0.90 and 0.64 respectively.

Isolation of the Saponin.—The defatted material after extraction with ether was soxhleted with alcohol (95%) for 40 hours. The dark brown syrupy mass obtained after removal of the solvent was repeatedly washed with ether (total 500 c.c.). The ether-insoluble gummy residue gave the tests for saponin.

Hydrolysis of the Saponin: Isolation of Oleanolic Acid.—The above residue was hydrolysed with 5% alcoholic hydrochloric acid for 4 hours. The hydrolysed product was taken up in ether after precipitation with water. The ether extract was washed with aqueous caustic soda (5%) and the sodio salt of the acid was acidified when the acid sapogenin was obtained as a white amorphous mass (yield 2.5 g.). This on repeated crystallisation from aqueous ethanol gave the pure compound, m.p. 304-308°. (Found: C, 78.90; H, 10.56. Calc. for $C_{30}H_{48}O_3$: C, 78.89; H, 10.59%).

Methyl Ester of the Acid.—The methyl ester of the above acid was prepared with diazomethane in the usual way and was purified by column chromatography on acid-washed alumina. The ester was then crystallised from acetone and finally from ethanol, m.p. 198-200°. (Found: C, 79.17; H, 10.58. Calc. for $C_{31}H_{50}O_3$: C, 79.10; H, 10.71%). It did not depress the m.p. of an authentic sample of methyl oleanolate. The above methyl ester gave an acetate, m.p. 222°. The melting point was not depressed when admixed with an authentic sample of acetylmethyl oleanolate. (Found: C, 77.39; H, 10.31. Calc. for $C_{33}H_{52}O_4$: C, 77.30; H, 10.22%).

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OXIDATION OF Mn^{II} BY PERSULPHATE IN SULPHURIC ACID MEDIUM

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Oxidation reaction of Mn^{II}, catalysed by Ag^{+}, has been studied, the kinetics being followed by means of a Klett-Summerson photoelectric colorimeter. The reaction is unimolecular with respect to the persulphate ion and zero-molecular with respect to the manganous ion; the reaction rate is directly proportional to the silver ion c ncentration. The velocity constants are of the same order as found for other persulphate oxidation reactions, catalysed by the univalent silver ion. All these facts point to the similar mechanism of the reaction. The reaction is likely to be complicated under different conditions due to the occurrence of simultaneous reactions, viz., decomposition of the persulphate catalysed by the silver ion, formation of hydrogen peroxide from persulphate and sulphuric acid, and the interaction of $Mn_2(SO_4)_3$ and H_2O_2.

The immediate oxidation product of Mn^{II} is trivalent manganese, which is unstable, and its solutions can be stabilised only in the presence of excess of acids. In strong sulphuric acid medium, the salt formed is red-coloured manganic sulphate, $Mn_2(SO_4)_3$. Taube (*J. Amer. Chem. Soc.*, 1947, **69**, 1418) obtained it from the interaction of Mn^{II} and MnO_2 and used it as a catalyst in the reaction between chlorine and oxalic acid. Davidson (*ibid.*, 1950, **72**, 4744) prepared the chloride complex of Mn^{III} by the permanganate oxidation in presence of hydrochloric acid. Oxalate complexes of Mn^{III}, in the reaction between permanganate and oxalate in the presence of manganous ion, have been reported by Gupta and Ghosh (*Z. physikal. Chem.*, under publication). Cartledge and Ericks (*J. Amer. Chem. Soc.*, 1936, **58**, 2061) prepared dioxalate and trioxalate complexes under specified conditions and studied their properties. Citrate complex of Mn^{III} has been reported by Cabrera and Del Rio (*Anal. real Soc., Espan., Fis. y Quim.*, 1953, **49B**, 263) and tartrate complex by Pérez and Garcia (*ibid.*, 1953, **49B**, 187). Recently Chakravarti and Ghosh (*Proc. Nat. Acad. Sci., India*, 1957, **26A**, 41) have obtained $Mn_2(SO_4)_3$ in 7.5*M*-H_2SO_4 by the dichromate oxidation of Mn^{II}.

Formation of stable $Mn_2(SO_4)_3$ in 3.6*M*-H_2SO_4 by the persulphate has already been reported by the authors (*Naturwiss*, 1958, **45**, 184). The oxidation is slow as such and, hence, it has been carried out in the presence of silver ions. The kinetics were studied at 22° by means of a Klett-Summerson photoelectric colorimeter. It was first necessary to confirm that the red-coloured compound formed by the persulphate oxidation of Mn^{II} was identical with $Mn_2(SO_4)_3$, obtained by dichromate (D. N. Chakravarti, Doctoral Thesis, 1957, Chapter 2, p. 82) or permanganate (Vogel, "A Text-book of Quantitative and Inorganic Analysis", 1953, p. 312) oxidation. An examination of these by the Unicam spectrophotometer gave the maximum absorption at 505 mμ for all the three differently prepared samples of $Mn_2(SO_4)_3$. Hence, filter No. 50 was used for colorimetric determination of the red-coloured compound. Beer's law was also found to be obeyed within the concentration range investigated.

EXPERIMENTAL

All the vessels used in the reaction were of Jena glass and the reaction vessel was coated outside by black Japan to eliminate any photochemical effect. The medium of reaction was water, redistilled from a quartz vessel.

All the chemicals used were of B.D.H.-A.R. quality. Sulphuric acid (*d* 1.84) was of A.R. quality from Basic and Scientific Chemicals Private Ltd., Calcutta.

Stock solutions of manganous sulphate and silver nitrate were prepared in the usual way and standardised by usual methods. Persulphate solutions were always freshly prepared by direct weighing and the strength checked by the arsenite (Gupta and Ghosh, *Anal. Chim. Acta*, 1957, **17**, 379) and Eckardt's (*Chem. News*, 1900, **81**, 38) method.

Known amounts of manganous sulphate, silver nitrate and concentrated sulphuric acid were taken in a reaction vessel and placed in a thermos at at 22°. Persulphate solution was kept separately. After these had attained the temperature of the bath, calculated quantity of the persulphate solution was run in the reaction vessel and shaken. At suitable invervals of time, portions of the reaction mixture were taken out and the colorimetric determinations were made. The colorimeter had been standardised previously against the sulphuric acid of the concentrations used in the reaction mixture. Persulphate and the manganous sulphate of the concentrations used had no absorption for filter No. 50.

To compensate the contraction in the volume of the reaction mixture due to addition of sulphuric acid, a calculated quantity of redistilled water was added to the reaction vessel prior to the additon of the persulphate. The temperture of the reaction mixture rose by 1° on the addition of the persulphate solution, but it fell almost to that of the bath within 10 minutes. This slight increase in the temperature in the initial stage could be neglected.

The reaction could not be studied to completion as Beer's law held good only approximately for higher concentrations of $Mn_2(SO_4)_3$ and also due to the limiting concentration of $Mn_2(SO_4)_3$ in solution at a particular H^+-ion concentration, given by the equilibrium,

$$Mn^{3+} + 2H_2O \rightleftharpoons Mn^{2+} + MnO_2 + 4H^+.$$

Hence with higher concentrations of $Mn_2(SO_4)_3$, formation of MnO_2 occurs, which vitiates the colorimetric readings, and too low a concentration of the persulphate tends to make the reaction very slow for study.

Table I records the calibration of the colorimeter for $Mn_2(SO_4)_3$ prepared from $MnSO_4$ and the permanganate in sulphuric acid of the concentration range $1.8M - 4.95M$. This also proves the validity of Beer's law.

TABLE I

Col. reading.	Conc. of $Mn_2(SO_4)_3$ from iodometry.	Factor for calc. of the conc. of $Mn_2(SO_4)_3$ in N from readings.
63.5	$1.17\times10^{-3}N$	
127	2.34	
254	4.68	$\frac{4.68\times10^{-3}}{254} = 1.85\times10^{-5}$.
510	9 36	

The reaction rate increases with the increase in the concentration of the persulphate and the reaction is unimolecular with respect to this ion because time of decomposition of any fraction of the persulphate is independent of its original concentration. The reaction is zero-molecular with respect to the manganous ion. Table II records the results of one experiment at 22°. The unimolecular constants were calculated from the relation

$$K = \frac{2.303}{t} \times \frac{1}{C_{Ag}} \log \frac{a}{a-x} \quad \ldots \quad \ldots \quad (1)$$

where a is the initial concentration, $a-x$, the concentration after time t (in minutes) of the persulphate and C_{Ag} is the concentration of the silver nitrate. Persulphate concentration was calculated from $Mn_2(SO_4)_3$ estimated.

TABLE II

$K_2S_2O_8 = 0.02M$. $MnSO_4 = 0.04M$. $H_2SO_4 = 3.60M$. $AgNO_3 = 0.016M$. Temp. = 22°.

Time.	Col. reading.	$Mn_2(SO_4)_3$.	$K_2S_2O_8$.	K unl. (min.$^{-1}$).	Time.	Col. reading.	$Mn_2(SO_4)_3$.	$K_2S_2O_8$.	K unl. (min.$^{-1}$).
0 min.	0	0	0.0200 M	...	45 min.	244	4.489×10^{-3}	0.01775 M	0.1653
5	33	$0.6071\times10^{-3}N$	0.01969	0.1928	50	270	4.968	0.01751	0.1658
10	64	1.178	0.01941	0.1870	55	292	5 372	0.01731	0.1640
15	93	1.711	0.01914	0.1822	60	315	5.795	0.01710	0.1631
20	117	2.153	0 01892	0 1727	65	340	6.256	0.01687	0.1637
25	149	2.742	0.01862	0.1773	70	363	6.679	0.01666	0.1630
30	170	3.127	0.01843	0.1688	80	400	7.360	0.01632	0.1587
35	200	3.680	0.01816	0.1722	90	452	8.316	0.01584	0.1618
40	224	4.121	0.01793	0.1694	100	500	9.752	0.01512	0.1748
								Average	0.1708

From Table II unimolecular constants appear gradually to decrease with the time and this may be ascribed to the decomposition of the persulphate, catalysed by the silver ions, and in accord with our observation that there is a slow and slight evolution of some gas in the reaction mixture. The gas could not be other than oxygen. Tables III and IV record some of the average values of the unimolecular constants with different concentrations of persulphate and of the manganous sulphate.

TABLE III

$K_2S_2O_8 = 0.02M$. $H_2SO_4 = 3.60M$. $AgNO_3 = 0.008M$.

Conc. of $MnSO_4(M)$	...	0.02	0.04	0.08
Unimol. const.	...	0.1689	0.1701	0.1717

TABLE IV

	$MnSO_4=0.04M.$	$H_2SO_4=3.60M.$	$AgNO_3=0.008M.$
Conc. of $K_2S_2O_8$ (M)	0.01	0.02	0.04
Unimol. const.	0.1739	0.1701	0.1756

The effect of varying the concentration of silver nitrate on the reaction rate constants is linear, as is evident from Table V.

TABLE V

	$K_2S_2O_8=0.02M.$	$MnSO_4=0.04M.$	$H_2SO_4=3.60M.$
$AgNO_3$ (M) ...	0.004	0.008	0.016
Unimol. const. ...	0.1677	0.1701	0.1705

In Table VI are shown the colorimetric readings using different concentrations of sulphuric acid.

TABLE VI

	$K_2S_2O_8=0.02M.$		$MnSO_4=0.02M.$		$AgNO_3=0.008M.$			
Time	H_2SO_4 concentration in molarity.							
	1.80.	2.70.	3.15.	3.60	4.05.	4.50.	4.95.	5.40
5 min.	12.5	14.5	14.5	17.6	16.5	18.5	20.0	
10	28.0	28.5	29.5	32.5	32.0	34.5	35.0	
15	40.5	43.5	43.5	46.0	47.0	49.0	48.5	
20	54.0	55.5	57.0	61.0	60.5	63.5	60.5	
25	68.0	68.5	70.5	73.5	74.5	75.5	71.5	
30	82.0	...	83.5	86.5	86.5	87.5	79.5	
35	94.5	95.0	97.0	100.0	99.0	98.5	87.5	
40	107.0	108.5	109.5	113.5	111.0	107.5	92.5	
45	120.0	121.0	121.5	125.0	122.5	116.5	96.5	
50	133.5	135.0	135.5	138.0	132.5	125.5	99.0	
55	147.0	147.0	148.0	150.0	142.5	133.5	101.5	
60	160.0	157.5	159.5	160.0	152.0	138.0	103 *	
70	184.5	183.5	184.0	181.0	169.5	148.5	105.0	
80	208.0	207.5	...	...	186.5	158.5	...	
90	232.0	230.5	...	222.0	204.5	168.0	108.5	
100	255.0	253.5	...	...	...	...	111	
K uni.	0.1589	0.1601	0.1629	0.1689	0.1636	0.1593	0.1582	

No. Colour.

* The average of the constants was taken only up to this reading.

It would appear that in the beginning, the colorimetric readings go on increasing with the concentration of the sulphuric acid, but reverse is true at the later stage of the reaction. Also considering all the concentrations of the sulphuric acid, the readings are maximum when the concentration of the sulphuric acid is 3.60 M, at the intervals of 35, 40, 45, 50 and 55 minutes. The slow increase in the colorimetric readings (in the later stage) above 3.6 M concentration of H_2SO_4, is probably due to the reaction of $Mn_2(SO_4)_3$ with H_2O_2 produced from the persulphate. It should be stated that the mixtures of the persulphate and sulphuric acid respond to the test for H_2O_2 above 3.6 M overall concentration of the sulphuric acid, below which negligible amounts of H_2O_2 are produced. The formation of H_2O_2 in 5.4M-H_2SO_4 is so sufficient as to consume all $Mn_2(SO_4)_3$ from the very start of the reaction. The sharp increase in the readings (in the later stage) below 3.6 M of H_2SO_4 may be due to the tendency of the reaction mixture forming

colloidal MnO_2 for want of sufficient acid to hold Mn^{III} in solution. It is evident from the average values of the unimolecular constants in Table VI and what has been said above, that the most suitable concentration of H_2SO_4 for the formation of $Mn_2(SO_4)_3$ is 3.6 *M*.

The reaction was also studied at 27° and 32°. Table VII records the average values of the unimolecular constants at these temperatures.

TABLE VII

$K_2S_2O_8 = 0.02M$. $MnSO_4 = 0.02M$. $H_2SO_4 = 3.60M$. $AgNO_3 = 0.008M$.

Temp. ...	22°	27°	32°
Unimol. const. ...	.1689	0.2319	0.3250

The heat of activation calculated by the Arrhenius equation gives the average value of 11670 calories for the range 22-32°. The graphical value was found to be 11740 calories which is in good agreement with the calculated value.

Calculation of the Frequency Factor A

A is given by the relation

$$\log A = \log K + E/2.303RT \quad \ldots (2)$$

where all the symbols have the usual significance. Using the average value of the energy of activation, the values of *A* have been calculated at different temperatures.

TABLE VIII

Temp. ...	22°	27°	32°	
$A \times 10^{-7}$ min^{-1} ...	8.009	7.875	7.993	Av. 7.959

Calculation of the Entropy of Activation

For a unimolecular reaction, the thermodynamic treatment gives

$$k = (kT/h)\, e^{\Delta S/R}\, e^{-E/RT} \quad \ldots (3)$$

where '*k*' is Boltzman's constant and '*h*' is Planck's constant.
From equations (2) and (3)

$$A = (kT/h)e^{-\Delta S/R} \quad \ldots (4)$$

and

$$kT/h \simeq 10^{13} \quad \ldots (5)$$

The energy of activation calculated from equation (4) is -31.37 E.U. All these calculations may be said to be true within the range of the reaction which has been studied here.

Mechanism

The unimolecularity of the reaction with respect to the persulphate ion, zero-molecularity with respect to the manganous ion and direct proportionality to silver-ion concentration, all point to a similar mechanism as advanced by the authors in an earlier paper (Gupta and Ghosh, *J. Inorg. Nuclear Chem.*, under publication). The value of the unimolecular constant is of the same order as for other reductants such as NH_3, NH_4^+, Cr^{3+} or VO^{2+}. The negative entropy of activation

suggests (Frost and Pearson, "Kinetics and Mechanism", John Wiley & Sons Inc., New York, 1953, Chapter 5, pp. 98-99) the reaction taking place between a charged ion and a neutral molecule or between similarly charged ions.

Actually the rate-determining step is between oppositely charged ions as is evident from the following mechanism :

$$S_2O_8^{2-} \rightleftharpoons 2SO_4^- \quad \ldots \quad \text{(rapid)} \quad \ldots \quad (i)$$

$$2SO_4^- + Ag^+ \rightarrow Ag^{3+} + 2SO_4^{2-} \quad \ldots \quad \text{(slow)} \quad \ldots \quad (ii)$$

$$Ag^{3+} + 2Mn^{2+} \rightarrow Ag^+ + 2Mn^{3+} \quad \ldots \quad \text{(fast)} \quad \ldots \quad (iii)$$

The rate-determining step is (*ii*).

From (*ii*) $\quad -(dc/dt) = k_2 [Ag^+][SO_4^-]^2$

Also from (*i*) $\quad K = [SO_4^-]^2/[S_2O_8^{2-}]$

where K is the equilibrium constant.

Hence $$-\frac{dc}{dt} = Kk_2 [S_2O_8^{2-}][Ag^+] = k[S_2O_8^{2-}];$$

where $k = Kk_2[Ag^+]$.

The experimentally measured constant is equal to $k/[Ag^+]$.

$$\therefore \quad k_2 = \frac{k}{[Ag^+]K} = \frac{\cdot 1689}{K}$$

[Now K will be small of the order of 10^{-8}]

$$\therefore \quad k_2 = \frac{\cdot 1689}{10^{-8}} = 1.689 \times 10^7 \text{ litres moles}^{-1} \text{ min}^{-1}.$$

Calculation of the frequency factor and the entropy of activation of the rate-determining step (*ii*) gives the values 13.35×10^{13} and 5.13 E.U. This indicates the reaction between oppositely charged ions. It must be seen here that the values do not support the generally accepted mechanism,

$$S_2O_8^{2-} + Ag^+ \rightarrow Ag^{3+} + 2SO_4^{2-},$$

because observed values of frequency factor and the entropy are low. This makes clear that the slow reaction step is not between $S_2O_8^{2-}$ and Ag^+, but between Ag^+ and some product of S_2O_8 which is negatively charged.

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BENZOYL CHLORIDE AS A POLAR SOLVENT. PART I. SOLUBILITIES OF SUBSTANCES AND THE FORMATION OF SOLVATES IN BENZOYL CHLORIDE

By Ram Chand Paul, Malkiat Singh Bains and Gurdev Singh

A quantitative determination of the solubilities of various chlorides at 30°±0.1° and a qualitative one for a number of organic bases, oxides and other salts in benzoyl chloride have been carried out. Formation of solvates with this solvent has also been studied.

Benzoyl chloride, with its moderately high dielectric constant (22.9 at 25°) (Errara, *J. Phys. Radium*, 1924, **5**, 309) and a convenient working range (m.p. -0.63°, b.p. 197°) is quite suitable for study as a non-aqueous solvent. As a knowledge of the solubilities of the various reactants and reaction products is necessary for this purpose, a quantitative determination of the solubilities of various chlorides at 30° ± 0.1° has been carried out, results of which are shown in Table I. The term 'insoluble' refers to a solubility of less than 0.1%.

Table I

Chloride.	Solubility (g./100 g. of solvent).	Colour.	Heat produced during mixing.
$HgCl_2$	0.8	Light yellow	Nil
$SnCl_2$	1.7	Reddish brown	Nil
$SnCl_4$	Freely miscible	Faint red	Considerable
BiOCl	0.85	Colorless	,,
$BiCl_3$	1.56	,,	Nil
$AsCl_3$	Freely miscible	,,	,,
$ZnCl_2$	0.1	,,	,,
SbOCl	13.03	Light brown	Appreciable
$SbCl_3$	160.00	Dark brown	Heat absorbed
PCl_3	Freely miscible	Colorless	Nil
$POCl_3$	,,	,,	,,
$PSCl_3$	,,	,,	,,
PCl_5	2.2	,,	,,
SCl_2	Freely miscible	Red	,,
S_2Cl_2	,,	,,	,,
$TeCl_4$	2.96	Light yellow	,,
$AlCl_3$	37.07	Dark brown	Appreciable
$SOCl_2$	Freely miscible	Colorless	Nil
$FeCl_3$	23.60	Dark brown	Appreciable

It has been observed that the strongly ionic compounds are practically insoluble in benzoyl chloride; thus, anhydrous chlorides of Hg^I Na, K, Li, ammonium, Pb^{II} Cd, Cu^{II}, Ag, Ni^{II}, Co^{II}, Mn, Ca, Ba and Sr are insoluble. The fact that benzoyl chloride has a comparatively low dielectric constant (cf. water, 81 at 18°) accounts for

* A preliminary note on the subject has already been published (*Curr. Sci.*, 1957, **26**, 391).

its being a poor solvent for the strongly ionic compounds. The chlorides, which are soluble, are generally the Lewis acids, or are capable of producing the Lewis acids on dissolution. Most of them produce coloured solutions, probably due to the formation of complexes, and quite a few form solid solvates. Qualitative experiments have shown that the solubility of these chlorides increases with a rise in temperature.

The solubility of a number of oxides and salts has also been studied qualitatively (Table II). Most of these substances are solvolysed to produce chlorides (Part II of this series). The solubility of such compounds indirectly depends upon the solubility of the corresponding chlorides in this solvent.

TABLE II

Soluble with reaction.		React to give insoluble chlorides.	Insoluble & unreactive
* Fairly soluble.	Sparingly soluble.		
Fe_2O_3	Bi_2O_3	CaO	Al_2O_3
Sb_2O_3	HgO	PbO	Cr_2O_3
Sb_2O_5	MgO	CdO	TiO_2
As_2O_3	ZnO	CuO	P_2O_5
$[(CH_3)_2N.C_6H_5, C_7H_7]Cl$	$(CH_3COO)_2Hg$	BaO	
$(C_6H_5CO)_2O$		$AgNO_3$	
		$NaNO_2$	
		KNO_3	
		KBr	
		KI	
		$CuCO_3$	
		$CdCO_3$	

* The terms 'sparingly soluble' and 'fairly soluble ' denote a solubility of less than 5% and 5-10% respectively.

A qualitative study of the solubility of organic bases like quinoline, pyridine, α- and β-picolines, dimethylaniline and diethylaniline has shown them to be appreciably soluble in benzoyl chloride and some of them form definite solvates with it.

Formation of Solvates.—The formation of monosolvates of aluminium chloride (Wilson and Fuller, *Ind. Eng. Chem.*, 1922, **14**, 406 ; Menschutkin, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1310), aluminium bromide (Menschutkin, *loc. cit.* ; *Chem. Zentrl.*, 1911, I, 481), gallium trichloride (Ulich and Heyne, *Z. physikal. Chem.*, 1941, **B49**, 284 ; Greenwood and Wade, *J. Chem. Soc.*, 1956, 1527), magnesium bromide (Menschutkin, *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 102), titanium tetrachloride (Cullinane, Chard and Leyshon, *J. Chem. Soc.*, 1952, 4106 ; Bertrand, *Bull. soc. chim.*, 1880, **33**, 403 ; 1881, **34**, 631), ferric chloride (Nencki, *Ber.*, 1899, **32**, 2414 ; Boeseken, *Rec. trav. chim.*, 1903, **22**, 315) and anhydrous sulphuric acid (Bergmann and Radt, *Ber.*, 1921, **54B**, 1652) with benzoyl chloride has already been reported. In the present investigation, the formation of solvates by benzoyl chloride with other chlorides has been studied. An examination of the solid phase, obtained in the solubility determination in the case of each chloride, has shown that electrovalent compounds are resistant towards solvate formation. Thus, anhydrous chlorides of Na, K, Li, NH_4,

Hg^{I}, Pb^{II}, Ca, Ba, Sr, Cu^{II}, Ni^{II}, Co^{II}, Cd and Ag do not combine with benzoyl chloride. Bi^{III}, Sb^{III} and P^{III}, P^{V}, Se^{IV}, Te^{IV} and Hg^{II} chlorides also do not form any solvate with this solvent.

Manganese chloride forms a flesh coloured monosolvate, $MnCl_2.C_6H_5COCl$ which, decomposes without melting. Magnesium oxide gives a white monosolvate, $MgO.C_6H_5COCl$. Seel (*Z. anorg. Chem.*, 1943, **252**, 24) reported the formation of a monosolvate of antimony pentachloride with benzoyl chloride, while studying the solvent properties of liquid sulphur dioxide. This compound has now been prepared by the interaction of benzoyl chloride and antimony pentachloride directly.

A large amount of heat is produced when zinc oxide or cupric oxide reacts with benzoyl chloride. Though the ultimate products in these cases, at higher temperatures, are pure metal chlorides (Part II of the series), an examination of the solid phase, obtained during the determination of the solubility of these substances at 30°, shows the formation of intermediate solvates, e g., $2\ ZnCl_2.\ 3\ (ZnO.2\ C_6H_5COCl)$ and $3\ CuCl_2.\ CuO.C_6H_5COCl$ respectively.

Ferric oxide, chromium oxide, aluminium oxide, cadmium oxide, lead oxide (PbO_2), titanium dioxide, arsenious oxide and phosphorus pentoxide do not form any solvate with this solvent.

Formation of a monosolvate of pyridine with benzoyl chloride has been reported by Adkins and Thompson (*J. Amer. Chem. Soc.*, 1949, **71**, 2242). Now quinoline also has been found to form a white crystalline disolvate, $C_9H_7N.2C_6H_5COCl$, when both the liquids are mixed together.

Experimental

Benzoyl chloride used in the present investigation was purified by collecting the distillate between 194° and 196°. This was again fractionated over dry magnesium oxide and the fraction distilling at 195°/740 mm was collected. Since benzoyl chloride is readily hydrolysed, carefully dried anhydrous substances have been used and their purity and anhydrous state checked by analysis.

Procedure.—A requisite quantity of the metal chloride along with benzoyl chloride (10-15 c.c.) was sealed in a dry ampoule, which was rotated in the thermostat at 30° ± 0.1° for about 48 hours to allow the mixture to attain equilibrium. The ampoule was then broken and the slurry was filtered quickly through a sintered glass funnel in a dry atmosphere. The solid was examined for the formation of solvates, while the solubility of the substance was determined by actual estimation of the cation from the filtrate (saturated solution) by the usual methods.

For the study of solvate formation, the solid phase was washed with benzoyl chloride and petroleum ether (b. p. 40-60°) successively and dried under vacuum. It was then analysed for the metal and chlorine and the formation of the solvates inferred.

In the case of the solvate of quinoline, the base was estimated by the Jackson and Smith method (*J. Amer. Chem. Soc.*, 1940, **62**, 544). The results of analyses are recorded in Table III.

TABLE III

Solvate.		Found.	Calc.
$MnCl_2.C_6H_5COCl$	Mn:	21.54	20.58
	Cl :	40.94	39.94
$MgO.C_6H_5COCl$	Mg :	13.20	13.46
	Cl :	19.83	19.63
$SbCl_5.C_6H_5COCl$	Sb :	27.70	27.69
	Cl :	48.52	48.43
$2\,ZnCl_2.\,3\,(ZnO.2C_6H_5COCl)$	Zn :	23.70	24.00
	Cl :	25.85	26.15
$3\,CuCl_2.\,CuO.C_6H_5COCl$	Cu :	40.48	40.85
	Cl :	39.85	39.92
$C_5H_7N.2C_6H_5COCl$	Cl :	17.21	17.32
	N :	3.36	3.41

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SPECTROPHOTOMETRIC STUDIES ON FERROUS COMPLEXES OF QUINOLINE- AND PYRIDINE-CARBOXYLIC ACIDS. PART II. FERROUS PICOLINATE SYSTEM

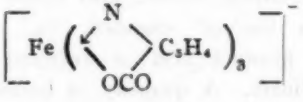
By Bireswar Banerjee and Privadaranjan Rây

The strongly coloured, highly soluble ferrous complex with picolinic acid forms the subject matter of the present investigation in respect of its usefulness for the estimation of iron. The coloured complex has been found to develop its maximum colour intensity between p_H 5.2 and 9. The presence of KCN, so also of pyridine to some extent, increases this colour intensity with an absorption maximum lying at about 440 mμ. The coloured system, with or without KCN, obeys Beer's law.

The composition of the coloured complex is given by 1 Fe^{II}: 3 acid, with an instability constant 5.07×10^{-12}. The complex thus acquires the character of a univalent anion.

In continuation of our previous communication (this *Journal*, 1958, **35**, 297) we are now in a position to report the results of our investigation on the highly coloured ferrous picolinate system. Picolinic acid was first employed by Majumdar and Sen (*Anal. Chim. Acta*, 1953, **8**, 369) for the colorimetric estimation of ferrous iron, and they also determined the composition of the coloured complex by Job's method (*Compt. rend.*, 1925, **180**, 928), which was given by $1Fe^{II}$: 2 acid. This seems to suggest that the complex must be a non-electrolyte; this cannot, however, be reconciled with its extreme solubility. The instability constant of the complex was found by Majumdar and Sen to be 4.23×10^{-5}. On the other hand, Shimra *et al.* (*J. Chem. Soc., Japan*, 1954, **75**, 44) showed that composition of the coloured ferrous picolinate complex should be represented by $1Fe^{II}$: 3 acid. This discrepancy in the results of the two sets of workers necessitated a re-investigation of the problem.

In the present work, the composition of the coloured complex in solution has been found to correspond to that given by the Japanese workers, namely $1Fe^{II}$: 3 acid, as shown below:



This can occur only as an anion in solution, which is supported by the fact that the colour intensity increases with the p_H of the solution and becomes constant in the alkaline region. Determination of the instability constant of the complex also leads to a value differing widely from that of Majumdar and Sen (*loc. cit.*) and is given by 5.07×10^{-12}.

The colour of ferrous picolinate, like that of ferrous quinaldinate, is also highly intensified by the addition of potassium cyanide and to some extent by pyridine.

The colour intensity in the presence of cyanide was employed by the previous workers (*loc. cit.*) for the colorimetric estimation of ferrous iron. In solutions containing cyanide, a molecule of picolinic acid is probably replaced by a corresponding number of cyanogen groups. As in the case of quinaldinic acid, the colour intensity of the ferrous picolinate system increases with the increasing amount of po'assium cyanide and then reaches a maximum and constant value, beyond which no further change occurs. The λ_{max} remains, however, unchanged, which is rather unusual. In the presence of a moderate or smaller amount of potassium cyanide, the colour of the ferrous picolinate system behaves similarly to that of ferrous quinaldinate with time. After 3 or 4 days a pink tint appears in the solution and the absorption maximum shifts towards the ultraviolet. In the presence of a large excess of KCN, the colour remains practically unchanged for several days.

Addition of pyridine also intensifies the colour of the ferrous picolinate complex in solution to a certain extent, but unlike potassium cyanide it does not lead to a maximum or constant value. The intensity of the colour continues to increase with the increasing amount of pyridine added, and finally the absorption maximum shifts rapidly towards the ultraviolet, when a certain concentration of pyridine in the system is exceeded.

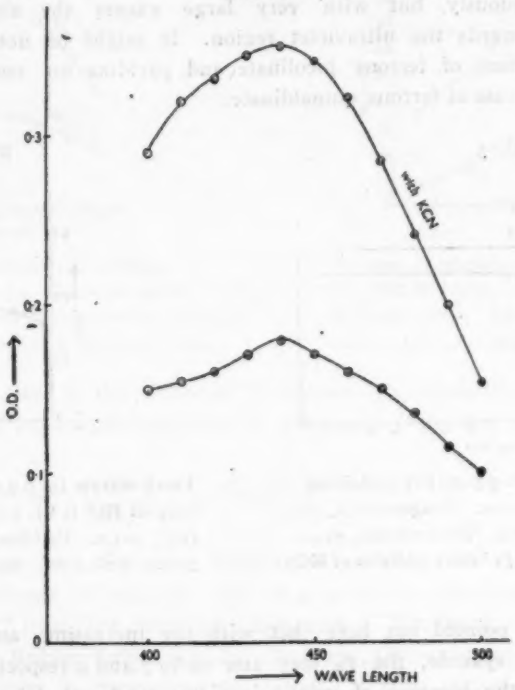
Experimental

Picolinic acid was prepared by the oxidation of α-picoline (Ramage and Clemo, *J. Chem. Soc.*, 1931, 440). A Unicam SP 600 spectrophotometer and guaranteed quality chemicals were employed for experimental work. The colour of the ferrous picolinate complex is yellow and the absorption maximum lies in the region of 440 mμ. The maximum colour formation occurs above p_H 5.2 and the colour intensity remains practically unchanged up to p_H 9. The system was found to obey Beer's law for concentrations above 5 p.p.m of ferrous ion, and gives a sensitivity of 0.056 γ/cm² (Sandell, "Colorimetric Determination of Traces of Metals", Interscience Publishers, New York, p. 47). Potassium cyanide intensifies the colour of the complex, though to a lesser extent than in the case of ferrous quinaldinate system, without any change in the wave-length for absorption maximum. The cyanide-containing system also obeys Beer's law and its sensitivity rises to 0.028 γ of ferrous ion/cm² (Sandell, *loc. cit.*). Three to four times the theoretical quantity of picolinic acid is required for the maximum colour development of ferrous picolinate. A quantity of potassium cyanide, at least 80 to 100 times that of ferrous ion present, is required for the maximum intensification of colour. The colour system with or without the cyanide or pyridine is quite stable at room temperature and remains almost unchanged for about 24 hours.

Wave-length of Absorption maximum (λ_{max}).—The same procedure as in the case of ferrous quinaldinate system (*loc. cit.*) was followed. The reagent blank and the iron solution (ferric nitrate + $NH_2OH.HCl$) separately showed negligible or no absorption at or about 440 mμ. Fig. 1 shows the optical density values

of the coloured complex at different wave-lengths with or without KCN. The colour formation is instantaneous as in the case of quinaldinic acid (*loc. cit.*).

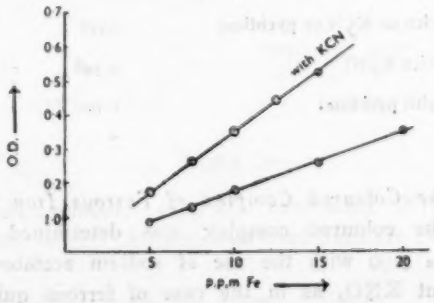
FIG. 1



Ferric nitrate (50 p.p.m of Fe), 10 c.c. $NH_2OH.HCl$ (5%), 5 c.c. Picolinic acid (1%), 10 c.c. KCN (1%), 10 c.c. Total volume, 50 c.c. Cell used, 1 cm.

Beer's Law.—The coloured complex of ferrous picolinate with or without cyanide obeys Beer's law. This is evident from the optical density values given in Fig. 2.

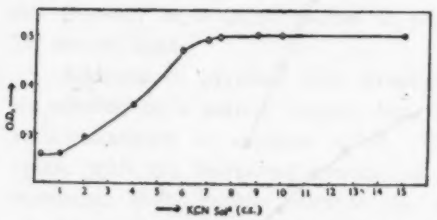
FIG. 2



Ferric nitrate (50 p.p.m Fe), x c.c. $NH_2OH.HCl$ (5%), 5 c.c. Reagent (1%), 10 c.c. KCN(1%), 10 c.c. Total volume, 50 c.c. Cell, 1 cm. 440 mμ.

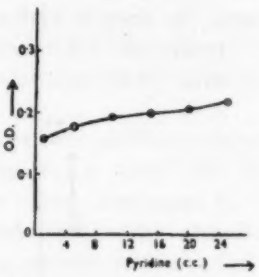
Influence of Cyanide and Pyridine Concentrations.—The effect of the concentration of cyanide and of pyridine on the coloured system is shown in Figs. 3 and 4 respectively. With the addition of pyridine the colour intensity at 440 mμ rises slowly and continuously, but with very large excess the absorption maximum shifts abruptly towards the ultraviolet region. It might be noted here that from concentrated solutions of ferrous picolinate and pyridine no compound could be isolated unlike the case of ferrous quinaldinate.

FIG. 3



Fe-amm. sulphate (70 p.p.m, Fe) containing $NH_2OH.HCl$ (1%), 10 c.c. Reagent (1%), 10 c.c. KCN (700 p.p.m), x c.c. Total volume, 50 c.c. Cell, 1 cm. mμ 440. p_H before addition of KCN, 6 (approx.).

FIG. 4



Ferric nitrate (50 p.p.m Fe), 10 c.c. NH_2OH HCl (5%), 5 c.c. Picolinic acid (1%), 10 c.c. Pyridine, x c.c. Total volume, 50 c.c. Cell, 1 cm. mμ 440.

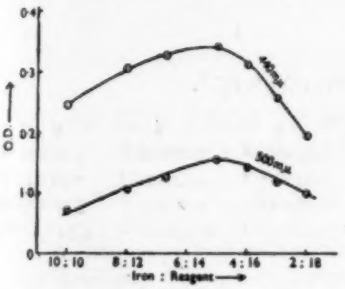
It should be pointed out here that with the increasing amount of pyridine and of potassium cyanide, the p_H may rise up to 7 and 9 respectively. As with the quinaldinic acid, the increase of colour intensity produced by potassium cyanide or pyridine is not due to this increase in the p_H value of the medium. This is clear from the following values of optical density for one and the same concentration of iron at the same p_H of solutions with KCN or pyridine and without any such addition.

[p_H 6.9, mμ 440, cell 1 cm, reagent in excess].

I. (with no KCN or pyridine)	0.178
II. (with KCN)	0.348
III. (with pyridine)	0.191

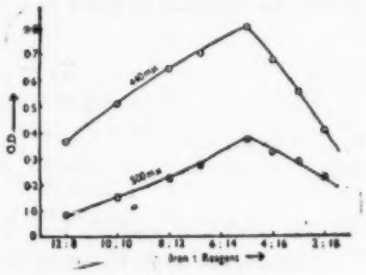
Composition of the Coloured Complex of Ferrous Iron with Picolinic Acid.—The composition of the coloured complex was determined spectrophotometrically by Job's method at p_H 5.99 with the use of sodium acetate—acetic acid buffer and in presence of sufficient KNO_3 as in the case of ferrous quinaldinate system. The results of measurement are shown in Fig. 5 (A, B). From the curves it is clear that the composition of the complex is represented by 1 Fe^{II} : 3 acid.

FIG. 5A



Fe-amm. sulphate (0.0025*M*) containing NH_2OH HCl (1%), *x* c.c. Picolinic acid (0.0025*M*), *y* c.c. KNO_3(1*M*) soln., 10 c.c. Buffer (5.99 p_H), 18 c.c. Total volume, 50 c.c. Cell used, 2 cm.

FIG. 5B



Fe-amm. sulphate (0.005*M*) containing NH_2OH.HCl (1%), *x* c.c. Picolinic acid (0.005*M*), *y* c.c. All other conditions are exactly the same as in Fig. 5A.

Instab lity Constant of the Coloured Complex.—The instability constant of the coloured complex of ferrous picolinate can be calculated from the following equation (cf. Part I, *loc. cit.*)

$$K_e = \frac{[Fe^{2+}]}{[(FeP_3)^-]} \times \frac{K_a^3\{[P_t]-3[(FeP_3)^-]\}^3}{K_a^3+[H^+]^3} \quad \ldots \quad (1)$$

All the symbols have the same significance as indicated in Part I (*loc. cit.*). P represents a molecule of picolinic acid or a picolinate ion and P_t, total picolinic acid. $K_a = 3.0 \times 10^{-6}$ from the literature (Hodgman, "Handbook of Chemistry and Physics", Chemical Rubber Publishing Co., Cleveland, Ohio, 1955-56, p. 1645), $[H^+]$ is obtained directly from p_H measurements, $[(FeP_3)^-]$ from optical density, and all the other factors are known from the experimental conditions. Tables IA and IB record the values of measurement for the coloured complex in equilibrium.

TABLE IA

Ferrous ammonium sulphate (0.002*M*) containing $NH_2OH.HCl$(1%), *x* c.c. Picolinic acid (0.005 *M*), *y* c.c. KNO_3(1 *M*) soln., 10 c.c., Buffer (p_H 5.99), 18 c.c. Cell, 2 cm. 440 mμ.

Picolinic acid (c.c.) ...	8	9	10(a)	11(b)	12(c)	13(d)	14
Fe-soln. (c.c.) ...	12	11	10	9	8	7	6
O.D. ...	0.406	0.467	0.502	0.519	0.528	0.498	0.458

TABLE IB

Ferrous ammonium sulphate (0.01 *M*) containing $NH_2OH.HCl$ (1%), *x* c.c. Picolinic acid (0.005*M*), *y* c.c. All the other conditions are exacty the same as in Table IA.

Picolinic acid (c.c.) ...	5(e)	6.0	6.65	7.5	8(f)	8.5	9(g)
Fe-soln. (c.c.) ...	5	4	3.35	2.5	2.0	1.5	1.0
O.D. ...	0.243	0.292	0.346	0.395	0.419	0.429	0.339

Now from the equation (1), K_c was calculated for a, b, c, d, e, f and g. The results are collected in Table II.

TABLE II

$K_a = 3 \times 10^{-6}$. $[H^+] = 0.1023 \times 10^{-5}$.

	a	b	c	d	e	f	g
P_t	3.00×10^{-3}	1.10×10^{-3}	1.20×10^{-3}	1.30×10^{-3}	5.00×10^{-4}	8.00×10^{-4}	9.00×10^{-4}
FeP_3	2.53×10^{-4}	2.61×10^{-4}	2.66×10^{-4}	2.50×10^{-4}	1.22×10^{-4}	2.11×10^{-4}	1.70×10^{-4}
Fe	1.47×10^{-4}	9.90×10^{-5}	5.40×10^{-5}	3.00×10^{-5}	8.78×10^{-4}	1.89×10^{-4}	3.00×10^{-5}
K_c	3.37×10^{-12}	5.01×10^{-12}	5.47×10^{-12}	8.28×10^{-12}	7.19×10^{-12}	1.73×10^{-12}	4.34×10^{-12}

Hence, the mean $K_c = 5.07 \times 10^{-12}$.

Majumdar and Sen (*loc. cit.*) gave, however, a value of 4.23×10^{-5} for K_c, assuming that the composition is given by $1Fe^I : 2$ acid on the basis of their experimental results, which we failed to confirm.

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ON THE STUDY OF REMOVAL OF RARE-EARTHS AND UX_1 FROM BERYLLIUM, ALUMINIUM, ZIRCONIUM AND URANIUM

By B. C. Purkayastha and M. Ganguli

An attempt has been made to remove rare-earths and UX_1 from uranium, beryllium, aluminium and zirconium. The major constituents concerned containing rare-earths are taken in acetic acid solutions and solid calcium oxalate monohydrate is added and shaken for sometime. A decontamination of 1 p.p.m. is easily achieved after two or more successive operations. The method can be claimed to be free from any complexities mentioned earlier (this *Journal*, 1957, **34**, 427).

In a previous communication (Purkayastha and Bhattacharyya, this *Journal*, 1957, **34**, 427), it was observed that calcium oxalate acted as a faithful carrier of rare-earths and thorium activities. The authors added some calcium and precipitated it as oxalate in acetic acid medium. The precipitate was found to carry most of the rare-earths and thorium activities. This property was used by the authors for various purposes.

The present investigation relates to attempts to remove rare-earths and thorium (UX_1) from some of the important materials, used in nuclear science, by simply shaking with solid calcium oxalate monohydrate in acetic acid medium. This procedure may solve the complexities which was previously encountered in precipitation procedure and also bring out some improvements in the possibility of its application as a general technique in this type of investigation. It was anticipated that UX_1 could be made completely removable from aged uranyl nitrate solutions by mere shaking with CaC_2O_4,H_2O. This procedure guards against the possibility of carrying out trace of uranium along with calcium and may help us to proceed on with larger quantity of uranium for removal of UX_1 and rare-earth activities, which was not possible in the previous investigation. The extent to which CaC_2O_4,H_2O goes into solution under experimental conditions and its removal from the parent uranyl ions in question are also the subject matter of study. With these objects in view, the present work was undertaken.

Experimental

Reagents used were mostly of AnalaR quality. Traces of iron from beryllium were removed by ether-extraction of the complex thiocyanate. Beryllium was then precipitated as hydroxide and dissolved in minimum quantity of HCl, which was then neutralised till precipitation. The precipitate of beryllium hydroxide was dissolved in glacial acetic acid and the medium was made 3*N* with respect to acetic acid.

In the case of zirconium, zirconium oxychloride was taken and dissolved in minimum quantity of HCl. It was then partially precipitated as hydroxide. The medium was made 3*N* with respect to acetic acid and kept for a few days till the precipitate went into solution.

In the cases of aluminium and uranium, the excess of mineral acid was neutralised and made $3N$ with respect to acetic acid. Uranyl nitrate used in removing UX_1 was of G.R.E.Merck quality.

Eu^{154}, Ca^{45} and carrier-free Y^{91} were supplied by Harwell, England, as chloride in HCl solution.

The solution, prepared as described above, which contained the radioactive indicators concerned in the process at the start of the preparation, was shaken for about an hour with solid calcium oxalate monohydrate. The solid was separated from solution by centrifuging. The solid calcium oxalate was washed and dissolved in HCl and the activity carried by it was measured by a liquid counter. The solution was further treated with calcium oxalate monohydrate and the same procedure was repeated till it was in a sense free from any activity.

Decontamination was studied by varying the quantities of the major constituents and minor constituents, and consequently the quantities of the scavenger was also varied (Table I).

The data relating to the quantitative separation of UX_1 from uranium by mere shaking with CaC_2O_4, H_2O are recorded in Table II.

The extent to which calcium oxalate went into solution under such experimental conditions and its decontamination from a desired element (say uranium) were also studied (Table III).

TABLE I

Use of CaC_2O_4, H_2O *in scavenging rare-earths from beryllium, aluminium, zirconium and uraninm.*

Major constituents in mg./50 c.c. (M).		$CaC_2O_4.H_2O$.	Minor constituents (in g./50 c.c.) (R).	Initial ratio (M:R).	M:R in soln. after subsequent shak'ng with CaC_2O_4, H_2O in operation number. 1.	2.	3.	4.
Be	350	550 mg.	1×10^{-4}Y	$1:2.8\times10^{-4}$	$1:1.6\times10^{-4}$	$1:7\times10^{-5}$	$1:1.7\times10^{-7}$	
	700	820	1×10^{-5}Y	$1:1.4\times10^{-5}$	$1:7.7\times10^{-7}$	$1:8.4\times10^{-9}$	...	
	700	1800	3×10^{-4}Eu	$1:4.3\times10^{-4}$	$1:1.3\times10^{-4}$	$1:1.1\times10^{-5}$	$1:2.2\times10^{-7}$	
Al	300	930	1×10^{-4}Y	$1:3.3\times10^{-4}$	$1:2.3\times10^{-4}$	$1:1\times10^{-4}$	$1:2.3\times10^{-5}$	$1:2.4\times10^{-5}$
	600	840	1×10^{-5}Y	$1:1.6\times10^{-5}$	$1:5.8\times10^{-7}$	$1:1.4\times10^{-8}$	...	
	600	2000	3×10^{-4}Eu	$1:50\times10^{-4}$	$1:1.7\times10^{-4}$	$1:5.9\times10^{-5}$	$1:1.1\times10^{-5}$	$1:4.4\times10^{-7}$
Zr	300	840	1×10^{-4}Y	$1:3.3\times10^{-4}$	$1:9.8\times10^{-5}$	$1:2.5\times10^{-7}$	...	
	300	840	1×10^{-5}Y	$1:3.3\times10^{-5}$	$1:5.9\times10^{-6}$	$1:2.5\times10^{-8}$	...	
	600	1600	3×10^{-4}Eu	$1:50\times10^{-4}$	$1:4.7\times10^{-5}$	$1:4.8\times10^{-6}$	$1:1.3\times10^{-7}$	
*U	600	1400	1×10^{-3}Y	$1:1.6\times10^{-3}$	$1:8.4\times10^{-4}$	$1:1.4\times10^{-4}$	$1:1.6\times10^{-5}$	$1:4\times10^{-6}$
	600	1200	1×10^{-4}Y	$1:1.6\times10^{-4}$	$1:10\times10^{-5}$	$1:3\times10^{-7}$		
	1200	2400	3×10^{-4}Eu	$1:2.5\times10^{-4}$	$1:3.4\times10^{-5}$	$1:4.1\times10^{-6}$	$1:4.3\times10^{-7}$	

* In case of uranium, UX_1 was previously separated and necessary precautions were taken to guard against any activity due to disintegration of U_1.

TABLE II

Decontamination of calcium from uranium by successive precipitation of uranium with CO_2-free NH_3.

Ca/U in soln. at the start.	Ratio of Ca/U in the precipitate in operation No. 1.	No. 2.	No. 3.
1:20	$1:2\times10^3$	$1:1.5\times10^3$	$1:1\times10^4$

TABLE III

Removal of thorium (UX_1) from uranium.

Uranium.	Inactive Th added.	CaC_2O_4, H_2O added.	% Removal or carrying in successive operations. 1.	2.	3.	4.	5.	6.
(1) 600 mg.	Nil	1.4 g.	91.0	10.0	0.002	...	...	...
(2) 2000	Nil	4.0	99.9	1.5	0.1	...	...	...
*(3) 600	1 mg.	1.6	37.0	0.28	0.25	10	0.02	0.001

* With appreciable amount of carrier added, decontamination becomes less sharp and it requires more successive operations than those in the previous case. The poor decontamination is presumably due to the complex oxalate ion-formation.

Ca^{45} was used as a radioactive indicator in the study of its decontamination. The oxalate ions were decomposed by nitric acid and the simple procedure of removing calcium from uranium by successive precipitation of uranium with CO_2-free NH_3 was taken recourse to. The results of our investigation are given in tabular forms.

DISCUSSION

In the previous communication (*loc.cit.*), the carrying of rare-earths by calcium oxalate monohydrate was studied by simple precipitation. The major constituents were carried by co-precipitating with CaC_2O_4, H_2O. The results are very encouraging with small quantities of the elements to be decontaminated. This is, however, not practicable nor economic with larger quantities, and also it involves more chemical operations.

The procedure, adopted by us, for removing rare-earths and thorium from the elements such as beryllium, aluminium, zirconium and uranium by mere shaking with solid calcium oxalate monohydrate, is free from any complexity. It requires minimum chemical operations in the procedure. In some aspects, it may be more convenient than the solvent extraction and other procedures which are used in separating rare-earths from the materials mentioned above, because here the minor constituents are being separated and the major ones remain in a convenient form.

It is also interesting to note that the quantitative removal of UX_1 from uranium without any appreciable uranyl ion adsorbed is a troublesome problem with respect

to larger quantity in the previous precipitation procedure, but this type of simple shaking procedure, as described by us, with solid calcium oxalate monohydrate does not seem to carry uranium to any considerable extent even in high concentration of uranyl ion.

It has been observed by us, specially in the case of uranium, that during operation a certain amount of calcium goes into the solution. A simple method of calcium and uranium separation was taken recourse to. Table III shows that the amount of calcium remaining is negligibly small. Uranium, thus freed from rare-earths and thorium, can be safely recommended for nuclear researches.

We have only attempted a simple method to separate calcium from uranium. Any other modern procedure may also be used in case of each of the elements from which rare-earths have been eliminated. One of the advantages of the method is that UX_1 can be safely and quantitatively removed from uranium, and the separation of calcium from uranium is, however, a simple issue.

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ON THE RELATION BETWEEN THE STABILITY CONSTANTS OF METAL CHELATES IN SOLUTION AND THE ELECTRONEGATIVITY OF THEIR METAL COMPONENTS

By K. A. Venkatachalam and M. B. Kabadi

The relation between the stability constants of metal chelates of doubly charged ions of Mn, Fe, Co, Ni and Cu in solution and their electronegativity has been discussed from thermodynamical consideration. A simple linear relation existing between $\sqrt{\log K_1}$ and χ has been postulated where K_1 is the first stability constant and χ, the 'selected' Gordy and Thomas electronegativity.

Several workers have tried to relate the values of log K_1 (where K_1 is the first stability constant of a metal chelate in solution) of the chelates of a series of metal ions with a given ligand with the fundamental properties of metal ions like ionisation potentials, electronegativity, ionic radius, etc. When the chelates formed by the doubly charged ions of Mn, Fe, Co, Ni and Cu, the log K_1 values of which conform to Irving-Williams' order (*J. Chem. Soc.*, 1953, 3192) in a large number of cases, are considered, the relations suggested so far reduce to the following :

(*i*). Linear correlation of log K_1 with the sum of the first and second ionisation potentials of the gaseous atoms, corresponding to the change, $M \rightarrow M^{2+} + 2e$, viz., I_1+I_2 (Irving and Williams, *Nature*, 1948, **162**, 746 ; Ackermann *et al.*, *ibid.*, 1949, **163**, 723).

(*ii*). Linear correlation with I_2, corresponding to the change, $M^+ \rightarrow M^{2+} + e$ (Calvin and Melchior, *J. Amer. Chem. Soc.*, 1948, **70**, 3270).

(*iii*). Straight line plot of log K_1 against χ, where χ is the Haissinsky electronegativity (* *J. Phys. Radium*, 1946, **7**, 7) of the bivalent metal M^{II} (* Van Uitert *et al.*, Paper VII, Chelate Compound Stabilities in the Dissolved State, Report NYO-3372, March 5, 1952).

(*iv*). Smooth plot of log K_1 against χ (Chapman, *Nature*, 1954, **174**, 887).

Figs. 1, 2 and 3 show the results of application of these relations to a few data drawn from Martell and Calvin ("Chemistry of the Metal Chelate Compounds", New York, Prentice-Hall, Inc., 1952). I_1+I_2 and I_2 are expressed in kcal., the necessary data being taken from Williams (*J. Phys. Chem.*, 1954, **58**, 123, Table II) and Latimer ("The Oxidation States of the Elements and their Potentials in Aqueous Solutions", 2nd ed., New York, Prentice-Hall, Inc., 1952) respectively. The electronegativities used are the "selected" values of Gordy and Thomas (*J. Chem. Phys.*, 1956, **24**, 439), which are in general agreement with the Haissinsky values (*loc. cit.*). For Fe only, the Haissinsky value 1.65 has been used so that the corresponding points do not overlap those for Co. It is seen that relation (*i*) yields the best straight lines, while no definite relation between log K_1 and χ arises.

* The original papers were not consulted.

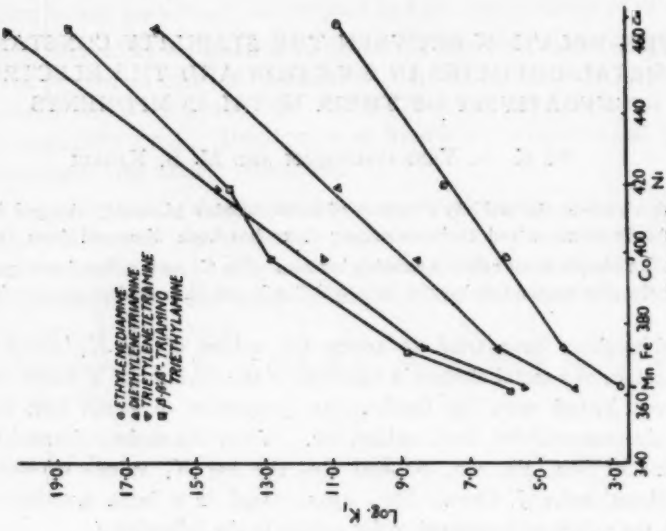

ETHYLENEDIAMINE
DIETHYLENETRIAMINE
TRIETHYLENETETRAMINE
β,β'β''-TRIAMINO TRIETHYLAMINE
log K1
19·0
17·0
15·0
13·0
11·0
9·0
7·0
5·0
3·0
340
360 Mn
Fe 380
Co 400
Ni 420
440
460 Cu
I2 in Kcal.

FIG. 2

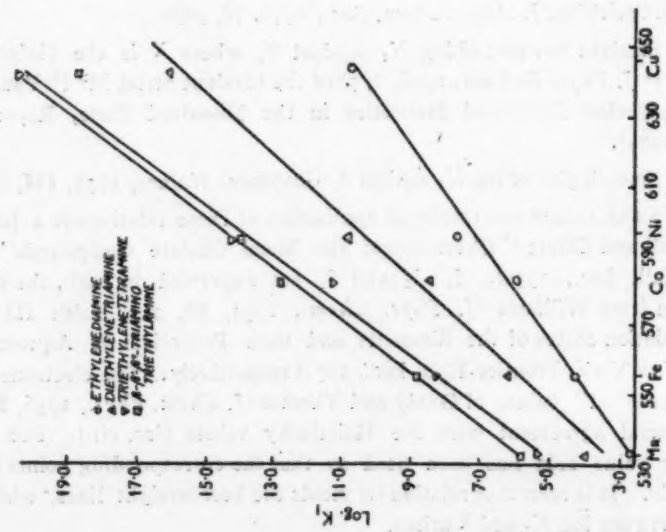
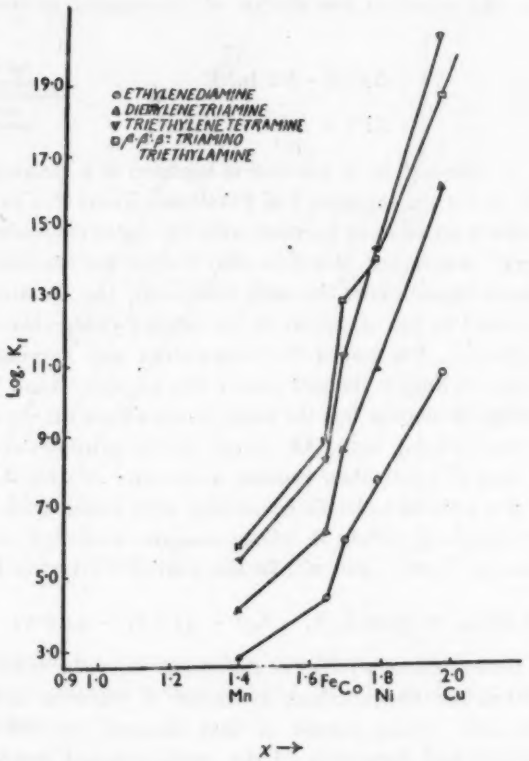

ETHYLENEDIAMINE
DIETHYLENETRIAMINE
TRIETHYLENETETRAMINE
β,β'β''-TRIAMINO TRIETHYLAMINE
log K1
19·0
17·0
15·0
13·0
11·0
9·0
7·0
5·0
3·0
530 Mn
550 Fe
570
Co 590
Ni 610
630
Cu 650
(I1+I2) in Kcal.

FIG. 1

FIG. 3



At the present state of our knowledge of chemical bonding, it is difficult to say which of the two properties, viz., ionisation potential or electronegativity of an atom, is more significant in this respect. Although ionisation potential is related to electronegativity by Mulliken's definition of electronegativity as $\chi = (I+E)/2$, where I is the ionisation potential and E, the electron affinity of the atom, the ionisation potential involved in this definition refers to the ionisation potential of the particular "valence state" of the atom, a quantity difficult to calculate and relation of which with the ionisation potential of the gaseous atom is not clearly known. However, electronegativity is related, at least semi-quantitatively, in the case of simple compounds to bond polarity, heat of formation etc., as shown by the classical work of Pauling. A definite relation between log K_1 and χ would therefore be of great interest.

The reaction between a metal ion M and a ligand L, e.g., the anion of a chelating acid or an amine, in a solution consists of the displacement of the solvation sheath around the metal ion followed by bond formation between the metal ion and the ligand. Log K of such a reaction, e.g.,

$$M(H_2O)_n + L \rightleftharpoons ML(H_2O)_{n-p} + p\,H_2O,$$

(where n and p are the numbers of water molecules, and charges are omitted for generality), measures the standard free energy of the reaction in view of the thermodynamic relation

$$\Delta F^\circ = -RT \ln. K.$$

Now

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ.$$

If the increase of entropy in a reaction is regarded as a measure of the resultant increase in "disorder" and if the suggestion of Frank and Evans (*J. Chem. Phys.*, 1945, **13**, 507) that the ions in an aqueous solution order the water molecules around them so as to form an "ice-berg" is accepted, it will be seen that for the reactions of a series of metal ions with the same ligand under the same conditions, the variations in the ΔS° values will be determined by the variations in the entropy change involved in the removal of the hydration sheath. For ions of the same charge and varying little in radius and atomic weight, like the doubly charged ions of Mn, Fe, Co, Ni and Cu, these entropy changes may be regarded as more or less the same, as seen from the equation of Powell and Latimer (*J. Chem. Phys.*, 1951, **19**, 1139) for the entropies of monoatomic ions in aqueous solution. Log K values then become a measure of the ΔH° values. The heat of formation of a gaseous molecule containing only single bonds and formed from the elements in their standard states, is given roughly according to Pauling ("The Nature of the Chemical Bond", 2nd ed., Ithaca, Cornell University Press, 1945, p. 62) by

$$Q_{kcal.} = 23.06 \Sigma (\chi_A - \chi_B)^2 - 55.1\, n_N - 24.2\, n_o$$

where χ_A and χ_B are the electronegativities of the atoms between which a single bond is formed, and n_N and n_o are the numbers of atoms of nitrogen and oxygen in the molecule. Now the ΔH° values consist of heat changes involved in the removal of the solvation sheath and formation of the metal—ligand bond. For the series considered here, the variable factor in both the heat terms is the metal ion only. It is therefore possible that in view of the Pauling relation $\sqrt{\log K_1}$ would bear a linear relation with χ, the electronegativity of the metal. This is shown to be true (Fig. 4) of the ligands considered in Figs. 1, 2 and 3, except for the values corresponding to Fe.

Comparison of Figs. 1 and 4 shows that the $\sqrt{\log K_1}$ against χ—plot yields straight lines which are as good as those obtained in the log K_1 against (I_1+I_2) plot, if the points for Fe are excluded. In view of the uncertainties in the data it is difficult to say which of these two relations is the better one. If both are assumed to be equally true, a simple relation between χ^2 and $(I_1 + I_2)$ may be expected for the series of elements considered. Fig. 5 shows this to be linear, the value for Fe being again an exception. It is interesting to note that if the value $\chi = 1.57$ is chosen for Fe^{II}, not only does it fall on the χ^2 against I_1+I_2 plot, but the log K_1 values for Fe also fall on the $\sqrt{\log K_1}$ against χ-plot.

The relation given here has been derived on a qualitative basis. It is realised that whereas the relation between Q and χ, as used here, applies to the reaction

$$M_{metal\ (standard\ state)} + L_{standard\ state} = ML_{gas},$$

FIG. 4

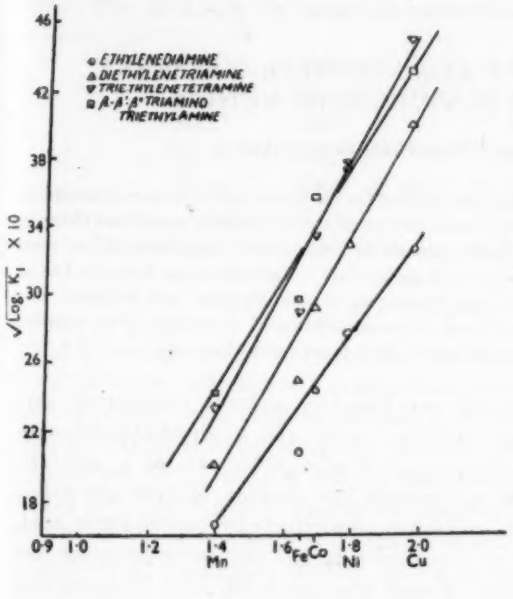
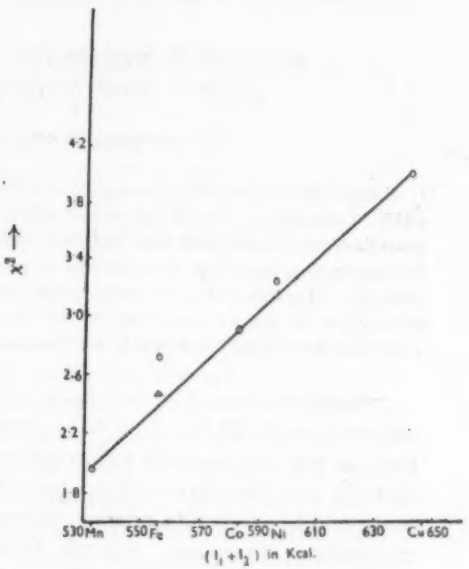


FIG. 5



(△ corresponding to Fe indicates $\chi = 1.57$)

log K_1 values refer to the corresponding reaction in solution. The thermochemical relations between the changes in heat content in the two reactions and other details will be published later.

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POTASSIUM PERSULPHATE AS A VOLUMETRIC REAGENT. PART I. THE IODINE MONOCHLORIDE METHOD

By Balwant Singh and Narinder Singh Ahuja

Potassium persulphate has been used as a volumetric reagent for the direct determination of arsenious oxide, tartar emetic, ferrous ammonium sulphate, ferrous ethylenediamine sulphate, mercurous chloride, potassium thiocyanate, hydrazine sulphate and hydroquinone in hydrochloric acid medium at room temperature, using iodine monochloride as a catalyst and pre-oxidiser. Chloroform has been used as an indicator. It is coloured violet owing to the liberation of iodine during the titration and becomes very pale yellow at the end-point due to the formation of iodine monochloride. Normality of the solution with respect to hydrochloric acid is kept between 6.0*N* and 7.5*N* in these redox titrations.

Marshall (*Proc. Roy. Soc. Edin.*, 1900, **23**, 163) found an aqueous solution of persulphuric acid ($H_2S_2O_8$) to be a strong oxidising agent and oxidised chromium to chromic acid and ammonia to nitrogen only in presence of a silver salt as a catalyst. Dittrich and Bollenbach (*Ber.*, 1905, **38**, 747) showed that chloride, bromide and iodide ions could be oxidised to chlorate, bromate and iodate respectively by persulphuric acid, catalysed by silver ions. Eckardt (*Chem. News*, 1900, **81**, 30) used persulphate for the quantitative oxidation of Fe^{II} to Fe^{III} at 80°. Kempf (*Ber.*, 1905, **38**, 3963) observed that oxalic acid was rapidly and quantitatively oxidised by persulphate in presence of a small amount of silver salt. Willard and Young (*J. Amer. Chem. Soc.*, 1928, **50**, 1379) determined Ce^{III} by oxidation with persulphate in presence of silver nitrate as catalyst, followed by electrometric titration of the excess persulphate with ferrous sulphate, potassium iodide or sodium nitrite. King and Jette (*ibid.*, 1930, **52**, 608) recommended persulphate as an oxidimetric standard in iodometry. Yost and Claussen (*ibid.*, 1931, **53**, 3349) oxidised vanadyl ion to vanadic acid with persulphate, using silver ion as catalyst. Dehn and Ballard (*ibid.*, 1932, **54**, 4264) used alkaline persulphate as an analytical reagent for the oxidation of cyanide, ferrocyanide, nitroprusside and thiocyanates to cyanic acid. Another volumetric method was suggested by Bright and Larrabee (*Bur. Standards J. Res.*, 1929, **3**, 573) and modified by Sandell *et al.* (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 256) in which Mn^{II} was oxidised to permanganate by persulphate in hot acid solution in presence of silver ions; permanganate so formed was estimated by sodium arsenite or by a mixture of sodium arsenite and sodium nitrite.

Of the several reductometric methods for the volumetric determination of persulphate, the iodometric and ferrometric methods are found to be most practicable from the points of view of rate of reaction, accuracy and simplicity. All the volumetric methods, proposed so far, are indirect and involve the oxidation of certain reducing agents with persulphate.

In the present study, potassium persulphate has been used as a volumetric reagent for the direct visual titrations of arsenious oxide, tartar emetic, ferrous ammonium sulphate, ferrous ethylenediamine sulphate, mercurous chloride, potassium thiocyanate, hydrazine sulphate and hydroquinone in hydrochloric acid medium at room temperature.

Iodine monochloride has been used as a catalyst and pre-oxidiser in these redox titrations. The oxidation by potassium persulphate proceeds according to the following reactions:

$$2\,S_2O_8^{2-} + As_2O_3 + 2H_2O = 4SO_4^{2-} + As_2O_5 + 4H^+$$
$$2S_2O_8^{2-} + Sb_2O_3 + 2H_2O = 4SO_4^{2-} + Sb_2O_5 + 4H^+$$
$$S_2O_8^{2-} + 2Fe^{2+} = 2SO_4^{2-} + 2Fe^{3+}$$
$$S_2O_8^{2-} + Hg_2^{2+} = 2SO_4^{2-} + 2Hg^{2+}$$
$$3S_2O_8^{2-} + CNS^- + 4H_2O = 7SO_4^{2-} + CN^- + 8H^+$$
$$2S_2O_8^{2-} + N_2H_4 = 4SO_4^{2-} + N_2 + 4H^+$$
$$S_2O_8^{2-} + C_6H_4(OH)_2 = 2SO_4^{2-} + C_6H_4O_2 + 2H^+$$

EXPERIMENTAL

A known amount of each substance was transferred to a conical flask and about 10 c.c. of water, sufficient HCl to keep the normality of solution between 6.0*N* and 7.5*N*, 5 c.c. of 0.02*M* iodine monochloride and 5 c.c. of chloroform were added. The mixture was cooled to room temperature and titrated with 0.05*M* potassium persulphate. The reagent was added from a burette until the solution, which was coloured with iodine, became pale yellow and the chloroform layer acquired a purple colour due to iodine. The flask was stoppered and vigorously shaken during the titration. Addition of small volumes of the persulphate solution was continued, shaking vigorously after each addition, till the chloroform layer was faintly violet. The persulphate was then added dropwise, with shaking after the addition of each drop, till the chloroform layer became very pale yellow. The end-point was very sharp. Several titrations were performed in each case. From the volume of potassium persulphate solution used, corresponding to the end-point in each titration, the amount of the substance was calculated. Some typical results, recorded in Table I, show that the substances listed above can be determined by direct titration with potassium persulphate.

TABLE I

Titration with 0.05*M*-$K_2S_2O_8$.

	Taken.	Found.
As_2O_3	0.0495 g.	0.0495 g.
	0.1246	0.1244
$K(SbO).C_4H_4O_6.0.5H_2O$	0.0835	0.0835
	0.2093	0.2091
$FeSO_4.(NH_4)_2SO_4.6H_2O$	0.2353	0.2353
	1.0195	1.0194
$FeSO_4.(CH_2.NH_3)_2SO_4.4H_2O$	0.2088	0.2088
	0.9761	0.9762
Hg_2Cl_2	0.1882	0.1880
	0.6023	0.6018
KCNS	0.0167	0.0167
	0.0365	0.0364
$NH_2.NH_2.H_2SO_4$	0.0295	0.0295
	0.0780	0.0780
$C_6H_4(OH)_2$	0.0486	0.0484
	0.1377	0.1374

All chemicals used in this investigation were of guaranteed purity. Ferrous ethylenediamine sulphate was prepared by the method of Caraway and Oesper (*J. Chem. Ed.*, 1947, **24**, 235). Potassium persulphate solution (0.05*M*) was standardised by the iodometric method of Gopala Rao *et al.* (*Proc. Nat. Inst. Sci. India*, 1945, **11**, 331 ; 1946, **12**, 277).

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PHOTOGRAPHIC SENSITISERS. PART II. MERO-DI- AND -TRI-CARBOCYANINES

By Birendra K. Patnaik and M. K. Rout

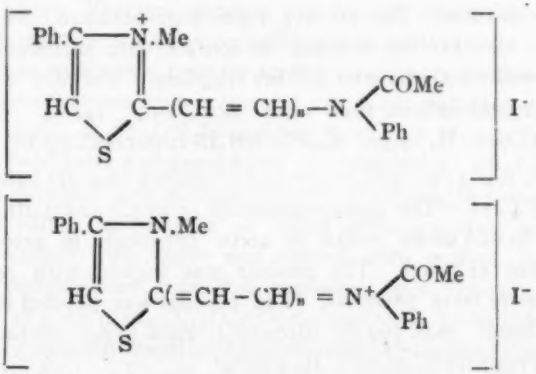
Quaternary methiodides of some 4-substituted 2-methylthiazoles have been condensed with β-anilinoacrolein anil hydrochloride and glutaconic aldehyde dianilide hydrochloride. The resulting acetanilidovinyl compounds have been prepared to study the shifts in absorption with each vinyl group addition. These reactive intermediates have also been condensed with ketomethylene compounds, yielding the corresponding mero-di- and -tri-carbocyanines.

From the absorption studies, vinylene homologous series may generally be divided into two categories: (*i*) members which carry an ionic charge and (*ii*) members which are uncharged, neutral molecules. In the latter category the substances are characterised by difference in λ_{max} between successive vinylene homologues which are, however, relatively small, usually less than 500 Å, and these differences diminish as the vinylene series is ascended. Thus in the series $CH_3(CH = CH)_n.COOH$, the difference in the value of λ_{max} (where $n = 1$ and $n = 2$) is 500 Å, that between $n = 2$ and $n = 3$ is 400 Å and the next shift is 330 Å. In the diphenylpropylene series $C_6H_5(CH = CH)_n.C_6H_5$, the shift from $n = 1$ to $n = 2$ is 330 Å and the succeeding shifts are 250, 270, 200, 210, 200 Å. In this series, deep colours, such as blue, are extremely difficult to attain, even with long conjugated chains.

Series in which the members have an ionic charge available for reasonance comprises mainly the polymethine dyes, of which the cyanines have been extensively investigated. The absorption of these series is characterised by vinylene shifts which are of the order of 1000 Å, and there is no decrease in the magnitude of these shifts as the series is ascended from methincyanines to heptamethincyanines. In these compounds therefore deep colour is commonly attained.

In the present investigation, a vinylene homologous series of thiacyanines has been prepared with a view to studying the shifts in absorption. Acetanilidovinyl compounds of the type I ($n = 1$)

(I)



have been reported by us earlier (this *Journal*, 1957, **34**, 543). These were prepared by condensing quaternary salts containing reactive methyl groups (4-phenyl-2-methylthiazole methiodide) with diphenylformamidine in acetic anhydride. In the present investigation, by replacing diphenylformamidine in the latter reaction by β-anilinoacrolein anil hydrochloride, acetanilido compounds such as (I : $n = 2$), and by glutaconic aldehyde dianilide hydrochloride, compounds such as (I : $n = 3$), have been successfully synthesised.

These acetanilido compounds have been subsequently condensed with reactive ketomethylene compounds (3-ethylrhodanine) in presence of acetic anhydride and fused sodium acetate, resulting in the formation of the corresponding merodicarbo- and merotricarbo-cyanines ($n = 2, 3$).

EXPERIMENTAL

2-(4-Acetanilido-1 : 3-butadienyl)-4-phenylthiazole Methiodide.—4-Phenyl-2-methylthiazole methiodide (3.17 g., 1 *M*) and β-anilinoacrolein anil hydrochloride (2.58 g., 1*M*) in acetic anhydride (12 c.c.) were refluxed for 1½ hrs. The dark product was treated with an excess of ether and the gummy mass was solidified by keeping it in contact with methanol. The product was recrystallised from acetic acid in needles, m.p. 200° (decomp.), yield 48%. (Found : C, 53.94 ; H, 4.21. $C_{22}H_{21}ON_2IS$ requires C, 54.11 ; II, 4.30%).

5-[4-(3-Methyl-4-phenylthiazolin-2-ylidene)-buten-1-ylidene]-3-ethyl-2-thiothiazolid-4-one.—The preceding methiodide (4.88 g., 1 *M*) and 3-ethyl-2-thiothiazolid-4-one (1.61 g., 1 *M*) were refluxed in acetic anhydride (15 c.c.) in presence of fused sodium acetate for about 3 hrs. The product after being treated with cold water was washed with acetone to remove tarry products. The acetone-washed product was finally recrystallised twice from hot methanol, m.p. 225-27° (decomp.), yield 42%. (Found : C, 58.88 ; H, 4.52. $C_{19}H_{16}ON_2S_3$ requires C, 59.06 ; H, 4.66%).

2-(4-Acetanilido-1 : 3-butadienyl) - 4 -p- methoxyphenylthiazole Methiodide.—4-*p*-Methoxyphenyl-2-methylthiazole methiodide (3.47 g.) and β-anilinoacrolein anil hydrochloride (2.58 g.) were refluxed in acetic anhydride for 2 hours. Excess of acetic anhydride was removed by distillation under reduced pressure and the dark product was treated with ether. The gummy mass, thus obtained, after being washed with acetone, was solidified by keeping in contact with methanol. The product, thus obtained, was sufficiently pure for further reactions. The pure material was obtained by two more recrystallisations from acetic acid, m.p. 142 43° (decomp.), yield 50%. (Found : C, 53.06 ; H, 4.31. $C_{23}H_{23}O_2N_2IS$ requires C, 53.28 ; H, 4.44%).

5-[4-(3-Methyl-4 - p - methoxyphenylthiazolin-2-ylidene)-buten-1-ylidene] - 3-ethyl-2-thiothiazolid-4-one.—The above methiodide (5.18 g.) and 3-ethyl-2-thiothiazolid-4-one (1.61 g.) were heated under reflux in acetic anhydride in presence of fused sodium acetate for about 2½ hours. The product was washed with cold water, followed by acetone to remove tarry products. The product was purified by two recrystallisations from hot methanol, m.p. 163-65° (decomp.), yield 38%. (Found : C, 57.49 ; H, 4.68. $C_{20}H_{20}O_2N_2S_3$ requires C, 57.69 ; H, 4.80%).

2-(4-*Acetanilido*-1 : 3-*butadienyl*) - 4 - p - *ethoxyphenylthiazole Methiodide*.—A mixture of 4-*p*-ethoxyphenyl-2-methylthiazole methiodide (3.61 g.) and β-anilinoacrolein anil hydrochloride (2.58 g.) was heated similarly as above. The dark residue was treated with ether and the product was washed with acetone and crystallised from methanol, m.p. 142-43° (decomp.), yield 45%. (Found : C, 54 02 ; H, 4.57. $C_{25}H_{25}O_2N_2IS$ requires C, 54.14 ; H, 4.70%).

5 - [4- (3-*Methyl*-4-p-*ethoxyphenylthiazolin*-2-*ylidene*) - *buten*-1-*ylidene*]-3 - *ethyl* - 2-*thiothiazolid* 4-*one*.—The preceding methiodide (5.32 g.) and 3-ethyl-2-thiothiazolid-4-one (1.61 g.) were refluxed in acetic anhydride in presence of fused sodium acetate for about one hour. The product after being washed with water was treated with a mixture of ether and methanol. The pure material was obtained by two recrystallisations from hot methanol, m.p. 193-95° (decomp.), yield 38%. (Found : C, 58.48; H, 5.02. $C_{21}H_{22}O_2N_2S_3$ requires C, 58.60 ; H, 5.11%).

2-(4-*Acetanilido*-1 : 3-*butadienyl*)-4-p-*bromophenylthiazole methiodide* was prepared by heating under reflux a mixture of 4-*p*-bromophenyl-2-methylthiazole methiodide (3.96 g.) and β-anilinoacrolein anil hydrochloride (2.58 g.) in acetic anhydride for 1½ hrs. After removing the excess of the solvent under reduced pressure, the product was extracted with methanol. Removal of methanol resulted in the separation of the product which was sufficiently pure for further reactions. The pure material was obtained by two more recrystallisations from acetic acid, m.p. 75-78° (decomp.), yield 52%. (Found : C. 46.38 ; H, 3.39. $C_{22}H_{20}ON_2BrIS$ requires C, 46.56 ; H, 3.52%).

5-[4- (3 -*Methyl*-4-p-*bromophenylthiazolin*-2-*ylidene*)-*buten* - 1 - *ylidene*]- 3 - *ethyl*-2-*thiothiazolid*-4-*one*.—The preceding methiodide (5.67 g.) and 3-ethyl-2-thiothiazolid-4-one (1.61 g.) were refluxed in acetic anhydride in presence of fused sodium acetate for 70 minutes. The product after being washed with water was washed with acetone. The acetone-washed product was finally recrystallised from hot mathanol, m.p. 151-52° (decomp.), yield 44%. (Found : C, 48.92 ; H, 3.54. $C_{19}H_{17}ON_2BrS_3$ requires C, 49.03 ; H, 3.65%).

2-(4-*Acetanilido*-1 : 3-*butadienyl*)-*benzothiazole Methiodide*.—2-Methylbenzothiazole methiodide (2.91 g.) and β-anilinoacrolein anil hydrochloride (2.58 g.) were refluxed in acetic anhydride for 1½ hrs. The dark product was treated repeatedly with ether and the gummy residue obtained was solidified by keeping it in contact with methanol. The product thus obtained was sufficiently pure for further reactions. The pure material was obtained by two recrystallisations from acetic acid, m.p. 160-62° (decomp.), yield 48%. (Found : C, 51.82; H, 4.02. $C_{20}H_{19}ON_2IS$ requires C, 51.95 ; H, 4.11%).

5-[4-(3-*Methylbenzothiazolin*-2-*ylidene*)-*buten* - 1 - *ylidene*]-3 - *ethyl*-2-*thiothiazolid* - 4-*one*.—The above methiodide (4.62 g.) and 3-ethyl-2-thiothiazolid-4-one (1.61 g.) were refluxed in acetic anhydride in presence of fused sodium acetate for 2 hrs. The product after being washed with water was treated with acetone to remove tarry products and finally recrystallised from hot methanol, m.p. 173-74° (decomp.), yield 42%. (Found : C, 56.45 ; H, 4.32. $C_{17}H_{16}ON_2S_3$ requires C, 56.66 ; H, 4.44%).

2-(6-*Acetanilido*-1 : 3 : 5-*hexatrienyl*)-4-*phenylthiazole Methiodide*.—4-Phenyl-2 - methylthiazole methiodide (3.17 g.) and glutaconic aldehyde dianilide hydrochloride

(2.84 g.) were refluxed in acetic anhydride for 70 minutes. Excess of the solvent was removed by distillation under reduced pressure and the dark product treated with ether, followed by acetone. The acetone-washed product was sufficiently pure for further reactions. The pure material was obtained by two recrystallisations from acetic acid, m.p. 182° (decomp.), yield 52%. (Found: C, 55.96; H, 4.41; I, 24.62. $C_{24}H_{23}ON_2IS$ requires C, 56.03; H, 4.47; I, 24.70%).

5-[6-(3-*Methyl*-4-*phenylthiazolin*-2-*ylidene*)-*hexa*-2:4-*dien*-1-*ylidene*]-3-*ethyl*-2-*thiothiazolid*-4-*one*.—The same procedure was followed by refluxing the preceding methiodide (5.14 g., 1 *M*) and 3-ethyl-2-thiothiazolid-4-one (1.61 g., 1 *M*) in acetic anhydride and fused sodium acetate. The product was isolated in the manner described earlier and recrystallised from hot methanol, m.p. 145-46° (decomp.), yield 45%. (Found: C, 50.87; H, 3.75. $C_{20}H_{20}ON_2S_3$ requires C, 51.33; H, 3.87%).

2 (6-*Acetanilido*-1:3:5-*hexatrienyl*)-4-p-*methoxyphenylthiazole Methiodide*.—4-*p*-Methoxyphenyl-2-methylthiazole methiodide (3.47 g.) and glutaconic aldehyde dianilide hydrochloride (2.84 g.) were refluxed in acetic anhydride for 70 minutes. The dark product was treated with excess of ether and the gummy mass so obtained was solidified by keeping it in contact with methanol. The product was recrystallised from acetic acid, m.p. 193-95° (decomp.), yield 50%. (Found: C, 55.01; H, 4.48. $C_{25}H_{25}O_2N_2IS$ requires C, 55.14; H, 4.59%).

5-[6-(3-*Methyl*-4-p-*methoxyphenylthiazolin*-2-*ylidene*)-*hexa*-2:4-*dien*-1-*ylidene*]-3-*ethyl*-2-*thiothiazolid*-4-*one*.—The preceding methiodide (5.44 g.) and 3-ethyl-2-thiothiazolid-4-one (1.61 g.) were refluxed in acetic anhydride and fused sodium acetate. The product after being washed with water was treated with acetone to remove tarry products. The acetone-washed product was finally recrystallised from hot methanol, m.p. 146-48° (decomp.), yield 44%. (Found: C, 59.62; H, 4.84. $C_{21}H_{22}O_2N_2S_3$ requires C, 59.73; H, 4.97%).

2-(6-*Acetanilido*-1:3:5-*hexatrienyl*)-4-p-*ethoxyphenylthiazole Methiodide*.—4-*p*-Ethoxyphenyl-2-methylthiazole methiodide (3.61 g.) and glutaconic aldehyde dianilide hydrochloride (2.84 g.) were refluxed in acetic anhydride for 1 hr. The excess of the solvent was removed under reduced pressure and the dark residue was treated with ether, followed by acetone. The acetone-washed product was sufficiently pure for further reactions. The pure material was obtained by two recrystallisations from acetic acid, m.p. 145-46° (decomp.), yield 48%. (Found: C, 55.68; H, 4.73. $C_{26}H_{27}O_2N_2IS$ requires C, 55.93; H, 4.84%).

5-[6-(3-*Methyl*-4-p-*ethoxyphenylthiazolin*-2-*ylidene*)-*hexa*-2:4-*dien*-1-*ylidene*]-3-*ethyl*-2-*thiothiazolid*-4-*one* was prepared in the same manner by refluxing the preceding methiodide (5.56 g.) and 3-ethyl-2-thiothiazolid-4-one (1.61 g.) in acetic anhydride and fused sodium acetate. The product after being washed with water, followed by acetone, was recrystallised from hot methanol, m.p. 178-80° (decomp.), yield 46%. (Found: C, 60.39, H, 5.13. $C_{22}H_{24}O_2N_2S_3$ requires C, 60.52; H, 5.26%).

2-(6-*Acetanilido*-1:3:5-*hexatrienyl*)-4-p-*bromophenylthiazole methiodide* was prepared from 4-*p*-bromophenyl-2-methylthiazole methiodide (3.96 g.) in the same way as the preceding ones. After removing the excess of acetic anhydride under reduced

pressure, the product was isolated in the manner described earlier and recrystallised from acetic acid, m.p. 87-88° (decomp.), yield 48%. (Found : C, 48.24 ; H, 3.60. $C_{24}H_{22}ON_2BrIS$ requires C, 48.56 ; H, 3.71%).

5-[6-(3-*Methyl*-4-p-*bromophenylthi zolin*-2-*ylidene*)-*hexa*-2 : 4-*dien*-1-*ylidene*]-3-*ethyl*-2-*thiothiazolid*-4-*one*.—The above methiodide (5.93 g.) and 3-ethyl-2-thiothiazolid-4-one (1.61 g.) were refluxed in acetic anhydride in presence of fused sodium acetate for 1 hr. The product was washed with water, followed by acetone to remove tarry products. The acetone-washed product was finally recrystallised from hot methanol, m.p. 222-23° (decomp.), yield 45%. (Found : C, 50.87 ; H, 3.75. $C_{20}H_{19}ON_2BrS_3$ requires C, 51.33 ; H, 3.87%).

2-(6-*Acetanilido*-1 : 3 : 5-*hexatrienyl*)-*benzothiazole Methiodide*.—2-Methylbenzothiazole methiodide (2.91 g.) and glutaconic aldehyde dianilide hydrochloride (2.84 g.) were refluxed in acetic anhydride for 70 minutes. The dark product was treated with ether and the gummy mass so obtained was solidified by keeping it in contact with methanol. The product, thus obtained, was sufficiently pure for further reactions. The pure material was obtained by recrystallisation from acetic acid, m.p. 163° (decomp.), yield 52%. (Found : C, 54.02 ; H, 4.22. $C_{22}H_{21}ON_2IS$ requires C, 54.11 ; H, 4.30%).

5-[6-(3-*Methylbenzothiazolin*-2-*ylidene*)-*hexa*-2 : 4-*dien*-1-*ylidene*]-3-*ethyl*-2-*thiothiazolid*-4-*one*.—The above methiodide (4.88 g.) and 3-ethyl-2-thiothiazolid-4-one (1.61 g.) were refluxed in acetic anhydride in presence of fused sodium acetate for 70 minutes. The product after being thoroughly washed with water, followed by acetone to remove tarry products, was finally recrystallised from hot methanol, m.p. 208-10° (decomp.), yield 44%. (Found : C, 58.88 ; H, 4.53. $C_{19}H_{18}ON_2S_3$ requires C, 59.06 ; H, 4.66%).

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STUDIES IN CARBOHYDRATES. PART VIII. STRUCTURE OF SWIETENOSE

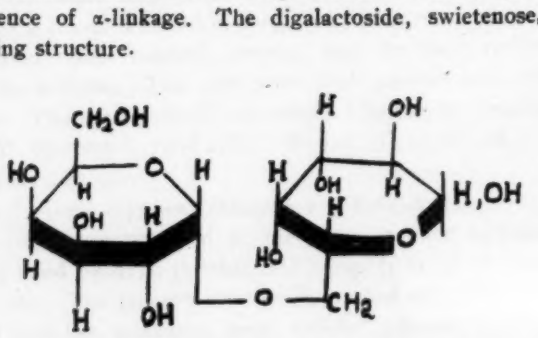
By T. R. Ingle and B. V. Bhide

Swietenose, a new digalactoside, obtained from Gum Mokha, has been further purified to a white hygroscopic powder. The crude digalactoside has been methylated. The methylated product on vacuum distillation furnishes octa-*O*-methyldigalactoside (m.p. 130-31°; $[\alpha]_D$ + 130.9°) which on hydrolysis affords an equimolecular mixture of 2:3:4:6-tetra- and 2:3:4-tri-*O*-methyl-D-galactoses. The structure of the digalactoside has been suggested from periodate oxidation as 6-*O*-α-galactopyranosido-D-galactoside.

Isolation of swietenose, a new digalactoside, from Gum Mokha (*Schrebera swietenioides*, N.O. Oleaceae) with 90% ethanol was reported previously (this *Journal*, 1954, **33**, 943). It was further purified by fractionating it on charcoal-hyflosupercel column (Whistler and Durso, *J. Amer. Chem. Soc.*, 1950, **72**, 677) using ethanol (5%) as an eluting solvent. The purified digalactoside fraction was concentrated to a syrup, which on trituration with absolute ethanol formed a white hygroscopic powder, $[\alpha]_D^{28}$ + 142.5° (*c*, 0.5% in water); its osazone had m.p. 193 94°.

The crude digalactoside was methylated by alkali and dimethyl sulphate and finally by Purdie's reagent. The methylated product, on distillation under reduced pressure, gave octa-*O*-methyldigalactoside, m.p. 130-31°, $[\alpha]_D^{28}$ + 130.9° (*c*, 2% in methanol). On hydrolysis of the methylated derivative, an equimolecular mixture of 2:3:4:6-tetra-*O*-methyl-D-galactose and 2:3:4-tri-*O*-methyl-D-galactose was obtained. The identity of these sugars was confirmed (1) by their physical properties and R_f values, (2) by running chromatograms with authentic specimens of these sugars, and (3) by preparing their anilides, characterising them by their physical constants and finding mixed m.p. with the authentic samples of anilides.

The high positive rotations of the digalactoside and its methylated derivative indicate the presence of α-linkage. The digalactoside, swietenose, should therefore possess the following structure.



6-*O*-α-D-Galactopyranosido-D-galactose.

The above structure has also been supported by its periodate oxidation. During oxidation, *five molecules* of formic acid were liberated and *six molecules* of periodate

were consumed for one molecule of digalactoside. It appears that the same digalactoside has been isolated by Turton *et al.* (*J. Amer. Chem. Soc.*, 1955, **77**, 2565) by the acid inversion of D-galactose.

EXPERIMENTAL

Isolation of Digalactoside.—Gum Mokha (25 g.) was extracted several times with 90% boiling ethanol till the residue did not show appreciable presence of mannitol chromatographically. It was dissolved in water, treated with charcoal and concentrated to a syrup. The concentrate was added to absolute alcohol (10 volumes), when the digalactoside precipitated as a white powder, yield 4 g. This was recognised as a crude digalactoside.

The crude digalactoside (2 g.) was completely separated from mannitol by fractionating it on charcoal-hyflosupercel column with elution by ethanol (5%). The pure digalactoside fraction was concentrated to a syrup under reduced pressure and added to absolute alcohol, when it was obtained as a white powder, yield 1.5 g. It did not crystallise, but it was found to be hygroscopic ; $[\alpha]_D^{28}$ +142.5° (*c*, 0.5% in water). It gave an osazone, m.p. 193-94°.

Methylation of the Digalactoside.—The crude digalactoside (10 g.) was methylated by dimethyl sulphate (150 c.c.) and sodium hydroxide (150 c.c., 40%) at room temperature four times. The reaction mixture was heated to 80° for 1 hour and extracted with chloroform (5 × 100 c.c.). The chloroform extract was washed with saturated sodium sulphate solution, dried over anhydrous magnesium sulphate and the solvent was removed, yield 10 g. (Found : OMe, 50.5%) ; $[\alpha]_D^{28}$ +125° (*c*, 2% in chloroform). The residue was methylated twice, by using methyl iodide (100 c.c.) and silver oxide (30 g.) each time, when a semi-solid was obtained. (Found : OMe, 55.5%) ; $[\alpha]_D^{28}$ +129.2° (*c*, 2% in chloroform). Further methylation did not raise the methoxyl content. When the product was subjected to vacuum distillation, octa-*O*-methyldigalactoside distilled at 280-90°/1.3 mm as a viscous syrup, which slowly solidified. It is soluble in ether, acetone, ethyl and methyl alcohols, benzene and sparingly soluble in petroleum ether ; yield 5 g. It crystallised in fine needles from ether-petroleum ether mixture, m.p. 130-31° ; $[\alpha]_D^{28}$ + 130.9° (*c*, 2% in methanol). (Found : C, 52.9 ; H, 8.7 ; OMe, 54.5. $C_{30}H_{58}O_{11}$ requires C, 52.83 ; H, 8.43 ; OMe, 54.63%).

Hydrolysis of Octa-O-methyldigalactoside.—The methylated sugar (0.8 g.) was hydrolysed by 1*N*-HCl at 90° for 12 hrs. Neutralisation with silver carbonate, followed by hydrogen sulphide treatment to remove Ag^+ ions, gave a filtrate, which on concentration furnished a mixture of methylated sugars as a syrup (0.75 g., 90%). Chromatographic examination showed the presence of two sugars, which were found to be 2 : 3 : 4 : 6-tetra-*O*-methyl-D-galactose and 2 : 3 : 4 tri-*O*-methyl-D-galactose by running authentic samples side by side. These sugars were separated on a cellulose column (70 × 6 cm) by eluting them with benzene-ethanol-water (169 : 47 : 15) mixture.

(1) 2 : 3 : 4 : 6-Tetra-*O*-methyl-D-galactose (0.33 g.) had OMe, 52.1%, $[\alpha]_D^{27}$ + 60.2 (*c*, 2% in ethanol). Calc. for $C_{10}H_{20}O_6$: OMe, 52.5% ; $[\alpha]_D$ +62.6° (Irvine and Cameron, *J. Chem. Soc.*, 1904, **85**, 1071). It gave an anilide which crystallised in wooly needles from alcohol, m.p. 193-94° (mixed m.p. 194°).

(2) 2 : 3 : 4-Tri-*O*-methyl-D-galactose (0.3 g.) had OMe, 41.3%; $[\alpha]_D^{28}$, + 142° (*c*, 2% in water) which finally changed to +114°. Calc. for $C_9H_{18}O_6$: OMe, 41.9%; $[\alpha]_D$ +142° → +114° (McCreath and Smith, *J. Chem. Soc.*, 1939, 389). It gave an anilide, m.p. 164-65°; $[\alpha]_D^{28}$ + 40° (*c*, 1% in MeOH); (OMe, 31.6; N, 4.9%); (mixed m.p. 165°).

TABLE I

Periodate oxidation of the digalactoside.

Time (hours)	0.5	1	2	4	6
Mols. of HIO_4 consumed for one mol. of					
Digalactoside	5.4	5.65	5.8	5.9	6.0
Melibiose	5.5	5.7	5.9	6.05	6.05
Lactose	4.05	4.7	5.05	5.1	5.1
Mols. of formic acid liberated for one mol. of					
Digalactoside	4.2	4.4	4.55	4.9	5.0
Melibiose	4.3	4.5	4.7	5.0	5.05
Lactose	2.7	2.8	3.0	3.1	3.15

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2-METHYLBENZIMIDAZOLE AS ANALYTICAL REAGENT FOR SILVER

By Prabhat K. Misra and Birendra K. Patnaik

2-Methylbenzimidazole has been used as an analytical reagent for the gravimetric estimation of silver. Influence of some of the cations has also been studied.

Feigl and Gleich (*Monatsh.*, 1928, **49**, 385) have shown that well-defined salts of copper, zinc and cadmium are formed with benzimidazole. The reaction between cobalt and benzimidazole has been used as a test for cobalt (Yagoda, *Microchem.*, 1938, **24**, 117). Preparation of some more copper and nickel complexes has also been reported by Ghosh (this *Journal*, 1951, **28**, 710). Benzotriazole, related to benzimidazole, and its 5-bromo derivative have been used by various workers (Remington and Meyer, Dissertation, Abst. No. 24, Ohio State Univ. Press, 1937; Tarasevich, *Vestnik*, Moscow Univ., 1946, **3**, No. 10, 161; Cherg, *Anal. Chem.*, 1954, **26**, 1038) as a reagent for gravimetric estimation of silver. Dutta (this *Journal*, 1956, **33**, 389) has also reported benzimidazole as an analytical reagent for silver. It was therefore considered of interest to use 2-methylbenzimidazole as a specific reagent for silver. In the present work, an attempt has also been made to study the interference of copper, nickel, cobalt and magnesium in the precipitation of silver in the presence of ammoniacal ethylenediamine tetra-acetate.

Experimental

The reagent, 2-methylbenzimidazole, was prepared by refluxing a mixture of *o*-phenylenediamine and glacial acetic acid at the boiling temperature.

Stock solutions of $AgNO_3$ were prepared and estimated by titrating with standard thiocyanate solutions using ferric alum as indicator. The reagent being insoluble in water, a solution of the reagent in minimum volume of alcohol was used.

To 10 c.c. of $AgNO_3$ solution (containing 0.1183 g. of Ag), diluted with 30-40 c.c. of water, was added nearly 10 c.c. of ammonia solution (20 c.c. of liquor ammonia made up to 100 c.c.) to bring the p_H to ~10, indicated by the universal indicator paper. The solution was then heated to 60-70° on a water-bath for about 5 minutes. An excess of warm alcoholic solution of the reagent (20 c.c. of 1%) was added dropwise with constant stirring till complete precipitation. The mixture was then digested on a water-bath for about 10 minutes and the precipitate filtered through a previously weighed G_3 crucible. The precipitate was washed with warm water and dried to a constant weight at 120°.

Composition of the Silver Complex.—A known amount of the silver complex was taken in a weighed porcelain crucible and heated till the organic contents burnt away. When the contents became greyish white, the crucible was heated to red heat for half an hour, cooled and the contents weighed.

TABLE I

Wt. of complex (g.)	...	0.1792	0.1194	0.1074
Ag found (g.)	...	0.0808	0.0540	0.0482

The above results lead to the conclusion that the silver complex may be formulated as $Ag(C_8H_7N_2)$.

The complex, when analysed, gave the following results. (Found : C, 40.01 ; H, 2.78 ; N, 11.57 ; Ag, 45.06. The proposed formula requires C, 40.20 ; H, 2.93 ; N, 11.72 ; Ag, 45.14%).

The influence of some of the cations in the estimation of silver by 2-methylbenzimidazole with or without the use of E.D.T.A. has also been studied. From Table II it appears that addition of ammoniacal E. D. T. A. solution prevents coprecipitation of foreign cations like Ni, Cu, etc. in the estimation of silver. Intereference study was carried out as shown below.

Procedure.—To 10 c.c. of the silver solution a constant amount of each of the interfering cations was added. For each cation two sets of experiments were performed. In the first set the complex was precipitated after the addition of ammoniacal E.D.T.A. solution and in the other, it was precipitated without the addition of E.D.T.A. The method of precipitation was the same as described above. The p_H was maintained at 10 and generally 2 to 3 times the theoretical amount of E.D.T.A., required to complex the particular metal, was used to hold the metal in solution.

Ammoniacal E.D.T.A. solution was prepared by dissolving the required amount of E.D.T.A. in nearly 10 c.c. of ammonia solution (20 c.c. liquor ammonia in 100 c.c.). Table II shows the amounts of complex formed with and without the addition of E.D.T.A.

TABLE II

Ions added.	Ag taken.	Weight of complex wth EDTA.	Weight of complex without EDTA.	Ag as calc from the complex with EDTA.
Cu^{2+}	0.1177 g.	0 2605 g.	0.2983 g.	0.1177 g.
	,,	0.2608	0.2986	0.1178
Ni^{2+}	0.0983	0 2190	0 2429	0.0986
	,,	0 2186	0.2432	0.0985
Mg^{2+}	0.0983	0.2190	0.2290	0.0987
	,,	0.2184	0.2286	0.0985
Co^{2+}	0.0963	0.2144	0.2424	0.0967
		0.2142	0.2420	0.0965

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SYNTHESIS OF α-ALKYL-γ-(4-METHOXY-3 CHLOROPHENYL)-BUTYRO LACTONES

By R. K. Genge and K. C. Kshatriya

α-Alkyl-β-(4-methoxy-3-chlor. benzoyl)-propionic acids, prepared by the Friedel-Crafts reaction between *o*-chloroanisole and alkylsuccinic anhydrides, have been reduced and lactonised to furnish the corresponding α-alkyl-γ-(4-methoxy-3-chlorophenyl)-butyro lactones.

Extending the work of Rosenmund and Schapiro (*Arch. Pharm.*, 1934, **272**, 313), Nargund *et al.* (*J. Univ. Bombay*, 1944, **12A**, Part V, 33) prepared α-alkyl-γ-(*p*-methoxyphenyl)- and α-alkyl-γ-(4-methoxy-3-tolyl)-butyro lactones. Buu-Hoï (*J. Org. Chem.*, 1950, **15**, 1060) found 6-*tert.*-butyl-1-chloro-2-naphthol to be effective against tapeworms. A chlorophenyl group is of much therapeutic importance as can be judged by its presence in compounds like DDT, Paludrine, Chloroquine, Oxychloroquine, Camoquine and Atebrine. Alkyl group also plays a very important part in endowing a compound with important physiological properties; it also helps in lowering the toxicity of the compound. Resorcinol is toxic, but *n*-hexylresorcinol is an important internal (urinary) antiseptic and shows anthelmintic properties against a variety of intestinal worms (Leonard, *J. Urol.*, 1924, **12**, 585; Lamson *et al.*, *Amer. J. Hyg.*, 1931, **13**, 568). The importance of alkyl chain is also evident in 5-heptyl-2-thiohydantoin which shows antitubercle properties (Eroelich *et al.*, *J. Amer. Chem. Soc.*, 1954, **76**, 3099).

It was therefore of interest to prepare phenylbutyro lactones containing a chlorine, a methoxy and an alkyl group. α-Alkyl-γ-(4-methoxy-3-chlorophenyl)-butyro lactones have been prepared and described in the present work.

o-Chloroanisole was condensed with alkylsuccinic anhydrides in presence of aluminium chloride when α-alkyl-β-(4-methoxy-3-chlorobenzoyl)-propionic acids were obtained.

The anhydride of a mono-substituted succinic acid, when condensed by the Friedel-Crafts reaction, may give rise to two isomeric α- and β-substituted acids. Mehta, Bokil and Nargund (*J. Univ. Bombay*, 1943, **12A**, Part III, 64) condensed anisole with alkylsuccinic anhydrides and obtained only one product, viz., α-alkyl-β-(4 methoxybenzoyl)-propionic acid; Mehta, Trivedi, Bokil and Nargund (*ibid.*, 1944, **12**, Part V, 35) similarly isolated only the α-acid in the case of condensation of alkylsuccinic anhydride with *o*-cresol methyl ethers.

The structure of the keto-acid has been assumed to be α-alkyl type as all keto-acids reacted with salicylaldehyde in the presence of dry hydrogen chloride in methyl

alcoholic solution to furnish crimson-red pyrillium derivatives, thus indicating the presence of $COCH_3$ grouping (Decker and Fallenberg, *Annalen*, 1907, **356**, 302 ; Perkin, Robinson and Turner, *J. Chem. Soc.*, 1908, **93**, 1085 ; Desai and Wali, *Proc. Ind. Acad. Sci.*, 1937, **6A**, 135).

The keto-acids, obtained by the condensation of *o*-chloroanisole with alkylsuccinic anhydrides, were oxidised by hot dilute alkaline potassium permanganate when an acid, m.p. 215°, was obtained. It was identified (mixed m.p.) as 4-methoxy-3-chlorobenzoic acid (Schall and Dralle, *Ber.*, 1884, **17**, 2529). Thus, the constitution of the keto-acids is assumed as α-alkyl-β-(4-methoxy-3-chlorobenzoyl)-propionic acids.

Ethyl esters of these keto acids were reduced by aluminium *iso*propoxide, and lactonisation of the resulting hydroxy-acids furnished α-alkyl-γ-(4-methoxy-3-chlorophenyl)-butyro lactones.

Experimental

n-Propyl-, *n*-butyl- and *n*-hexyl-succinic acids were prepared by the condensation of *n*-propyl, *n*-butyl and *n*-hexyl halides with malonic ester and ethyl chloroacetate and subsequent hydrolysis and decarboxylation. Methyl-, ethyl- and *n*-amyl-succinic acids were prepared by the condensation of ethyl α-halo-propionate,-butyrate and -heptylate with ethyl malonate and subsequent hydrolysis and decarboxylation.

α-Alkyl-β-(4-methoxy-3-chlorobenzoyl)-propionic Acids.—Alkylsuccinic anhydride (0.1*M*) was condensed in cold with *o*-chloroanisole (0.1*M*) by the Friedel-Crafts reaction, using a mixture of tetrachloro-ethane (80 c.c.) and nitrobenzene (20 c.c.) as solvent. After the addition of aluminium chloride (0.2*M*), the reaction mixture was kept for 24 hours in a cold water-bath. The reaction mixture was decomposed with ice and HCl. The solvent mixture was removed by steam distillation and the solid product obtained on cooling was filtered. The keto-acids were purified through their sodium salts.

α-Alkyl-γ-(4-methoxy-3-chlorophenyl)-butyro Lactones.—Ethyl α-alkyl-β-(4-methoxy-3-chlorobenzoyl)-propionate (0.03*M*) was refluxed with aluminium *iso*propoxide (0.03*M*) in dry *iso*propyl alcohol (30 c.c.) till the distillate was free of acetone (Roger Adams, "Org. Reactions", Vol. II, p. 196). After removal of *iso*propyl alcohol, HCl (dil.) was added and the organic layer separating was refluxed with alcoholic sodium hydroxide (30 c.c., 20% in 15 c.c. EtOH). After distilling off alcohol, the residue was diluted with water and the neutral impurities were removed with ether. The solution was then acidified with 25% H_2SO_4 (dil.) and more of the acid was added so as to bring the concentration of the acid to about 15%. It was heated on a water-bath for 2 hours. The product obtained on cooling was kept over a saturated solution of sodium bicarbonate for 24 hours so as to remove the acidic impurities from the lactone. If the product obtained was a liquid, it was extracted with ether and washed with sodium bicarbonate solution (5%), followed with water. The ether extract was dried over anhydrous sodium sulphate. Ether was removed and the residue was distilled under reduced pressure. In case of solids, the product was dried and crystallised from a suitable solvent. The lactones were obtained in 50 to 60% yield.

The compounds are tabulated in Tables I and II.

TABLE I

PA denotes -β-(4-methoxy-3-chlorobenzoyl)-propionic acid.

D.N.P. ,, dinitrophenylhydrazone.

No.	Name of the compound.	Mol. formula.	Properties.	% Chlorine. Found.	Calc.
1	α-Methyl-PA	$C_{12}H_{13}O_4Cl$	Needles from hot water, m.p. 140°.	14.0 (253.2)	13.8 (256.5)
2	Ethyl ester of (1)	$C_{14}H_{17}O_4Cl$	Liquid, b.p. 214-17°/8 mm. n_D^{28}, 1.524.	12.7	12.4
3	Semicarbazone of (1)	$C_{13}H_{16}O_4N_3Cl$	Needles from dil. alcohol, m.p. 165°.	11.5 (315.3)	11.3 (313.5)
4	α-Ethyl-PA	$C_{13}H_{15}O_4Cl$	Do from benzene, m.p. 129°.	13.3 (269)	13.1 (270.5)
5	Ethyl ester of (4)	$C_{15}H_{19}O_4Cl$	Liquid, b.p. 220-25°/6 mm. n_D^{28}, 1.53.	12.2	11 9
6	Oxime of (4)	$C_{13}H_{16}O_4NCl$	Needles from dil. acetic acid, m.p. 139°.	12.7	12.4
7	α-n-Propyl-PA	$C_{14}H_{17}O_4Cl$	Needles from benzene-petrol, m.p. 102°.	12.6 (285.9)	12.5 (284.5)
8	Ethyl ester (7)	$C_{16}H_{21}O_4Cl$	Liquid, b.p. 221-25°/8 mm. n_D^{28}, 1.525.	11.6	11.4
9	Oxime of (7)	$C_{14}H_{18}O_4NCl$	Needles from dil. acetic acid, m.p. 140°.	12.1	11.9
10	α-n-Butyl-PA	$C_{15}H_{19}O_4Cl$	Do from hot water, m.p. 100°	12.1 (300.4)	11.9 (2 8.5)
11	Ethyl ester of (10)	$C_{17}H_{23}O_4Cl$	Liquid, b.p. 216-30°/8 mm. n_D^{28}, 1.516.	11.1	10.9
12	2:4-D.N.P. of (10)	$C_{21}H_{23}O_7N_4Cl$	Yellow needles from EtOH, m.p. 213°.	7.6	7.4
13	α-n-Amyl-PA	$C_{16}H_{21}O_4Cl$	Needles from benzene-petrol, m.p. 98°.	11.5 (310.3)	11.3 (312.5)
14	Ethyl ester of (13)	$C_{18}H_{25}O_4Cl$	Liquid, b.p 244-47°/5 mm. n_D^{28}, 1.458.	10.6	10.4
15	2:4-D.N.P. of (13)	$C_{22}H_{25}O_7N_4Cl$	Yellow needles from EtOH, m.p. 208°	7.3	7.2
16	α-n-Hexyl-PA	$C_{17}H_{23}O_4Cl$	Needles from benzene, m.p. 129°.	11.1 (325.0)	10.9 (326 5)
17	Ethyl ester of (16)	$C_{19}H_{27}O_4Cl$	Liquid, b.p. 253-57°/8 mm. n_D^{28}, 1.456.	10.2	10 0
18	2:4-D.N.P. of (16)	$C_{23}H_{27}O_7N_4Cl$	Yellow needles from EtOH, m.p. 182°.	7.2	7.0

N.B. Figures in parentheses in last two columns refer to equiv. weights.

TABLE II

No.	Alkyl-γ-(4-methoxy-3-chlorophenyl)-butyro lactones.	Formula.	Properties.	% Chlorine. Found.	% Chlorine. Calc.	Equiv-wt. Found.	Equiv-wt. Calc.
1	α-Methyl-	$C_{12}H_{13}O_3Cl$	Liquid, b.p. 205-10°/8 mm. n_D^{40}, 1.534.	14.9	14.7	237.2	240.5
2	α-Ethyl-	$C_{13}H_{15}O_3Cl$	Plates from dilute alcohol, m.p. 85°.	14.2	13.9	252.7	254.5
3	α-*n*-Propyl-	$C_{14}H_{17}O_3Cl$	Needles from dilute alcohol, m.p. 88°.	13.4	13.2	271.0	268.5
4	α-*n*-Butyl-	$C_{15}H_{19}O_3Cl$	Plates from dilute alcohol, m.p. 89°.	12.7	12.6	280.0	282.5
5	α-*n*-Amyl-	$C_{16}H_{21}O_3Cl$	Plates from alcohol, m.p. 92°.	12.2	12.0	294.8	296.5
6	α-*n*-Hexyl-	$C_{17}H_{23}O_3Cl$	Do, m.p. 89°.	11.7	11.4	309.0	310.5

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SYNTHESIS OF α-ALKYL-γ-(2-METHOXY-5-CHLOROPHENYL)-BUTYRO LACTONES

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α-Alkyl-β-(2-methoxy-5-chlorobenzoyl)-propionic acids, prepared by the Friedel-Crafts reaction between *p*-chloroanisole and alkylsuccinic anhydrides, have been reduced and lactonised to furnish the correspond.ng α-alkyl-γ (2-methoxy-5-chlorophenyl)-butyro lactones.

In continuation with the work described in previous paper (this *issue*, p. 521) α-alkyl-γ-(2-methoxy-5-chlorophenyl)-butyro lactones have been synthesised.

p-Chloroanisole was condensed with alkylsuccinic anhydrides in the presence of aluminium chloride in acetylene tetrachloride and nitrobenzene solvent to obtain α-alkyl-β-(2-methoxy-5-chlorobenzoyl)-propionic acids. Except in the case of methylsuccinic anhydride, with other anhydrides the products obtained were partially demethylated. Such demethylation has been observed in the succinoylation of pyrogalloi trimethyl ether when β-(2-hydroxy-3 : 4-dimethoxybenzoyl)-propionic acid instead of (2 : 3 : 4-trimethoxybenzoyl)-propionic acid was obtained (Bargellini and Giua, *Gazzetta*, 1912, **42**, 197 ; Manske and Holmes, *J. Amer. Chem. Soc.* 1945, **67**, 95 ; Dalal, Bokil and Nargund, *J. Univ. Bombay*, 1939, **8**, Part II, 203 ; Mitter and De, this *Journal*, 1939, **16**, 35). Therefore these α-alkyl-β-(2-methoxy-5-chlorobenzoyl)-propionic acids were prepared by any of the following methods :

(*a*). Pure α-alkyl-β-(2-hydroxy-5-chlorobenzoyl)-propionic acids were obtained by the condensation of *p*-chlorophenol with alkylsuccinic anhydrides in acetylene tetrachloride solvent and these were methylated by dimethyl sulphate in alkali solution. α-Ethyl-, α-*n*-propyl- and α-*n*-butyl-β-(2-methoxy-5-chlorobenzoyl)-propionic acids were prepared by this method.

(*b*). The mixed acids obtained in the condensation of *p*-chloroanisole with alkylsuccinic anhydride were esterified and the mixed esters were methylated by dimethyl sulphate in presence of anhydrous potassium carbonate in dry acetone solution. The product on hydrolysis gave α-alkyl-β-(2-methoxy-5-chlorobenzoyl)-propionic acid. α-*n*-Hexyl acid was prepared by this method.

By analogy with the work described in the previous paper (*loc. cit.*), the structures of the keto-acids have been assumed to be α-alkyl type.

On oxidation with alkaline potassium permanganate, the keto-acids gave an acid (m.p. 81°-82°) which was identical with (mixed m.p.) methyl ether of 5-chlorosalicylic acid (Peratoner and Condorelli, *Gazzetta*, 1898, **28**, 211). Thus, these keto-acids are α-alkyl-β-(2-methoxy-5-chlorobenzoyl)-propionic acids.

Experimental

The condensation of *p*-chloroanisole with alkylsuccinic anhydride was carried out as described in the previous paper (*loc. cit.*).

Condensation of p-*Chlorophenol with Alkylsuccinic Anhydride.*—*p*-Chlorophenol (12.6 g., 0.1 *M*), alkylsuccinic anhydride (0.1 *M*) and tetrachloroethane (75 c.c.) were taken in a round-bottomed flask fitted with a condenser carrying a calcium chloride guard tube. To the cooled reaction mixture aluminium chloride (27 g., 0.2 *M*) was added in small lots with stirring. The mixture was heated in an oil-bath for about 3 hours at 120°. It was cooled and decomposed with ice and HCl and α-alkyl-β-(2-hydroxy-5-chlorobenzoyl)-propionic acid was isolated as usual. The methylation of α-alkyl-β-(2-hydroxy-5-chlorobenzoyl)-propionic acid was done by dimethyl sulphate as described by Trivedi and Nargund (*J. Univ. Bombay*, 1942, **11**, Part III, 127).

α-n-*Hexyl-β-(2-methoxy-5-chlorobenzoyl)-propionic Acid.*—The mixed keto-acids, obtained in the condensation of *n*-hexylsuccinic anhydride (18.4 g., 0.1 *M*) with *p*-chloroanisole (12.6 g., 0.1 *M*), were esterfied as usual. The mixed ester (9.0 g.), anhydrous K_2CO_3 (9 g.) dry acetone (40 c.c.) and dimethyl sulphate (4.0 g.) were refluxed on a water-bath for 12 hours. Acetone was removed and the residue was hydrolysed with alcoholic KOH solution (10%, 30 c.c.) by boiling for 4 hours. Alcohol was distilled off on a water-bath and the residue was diluted with water and acidified when α-*n*-hexyl-β-(2-methoxy 5-chlorobenzoyl)-propionic acid separated.

The reduction of α-alkyl-β-(2-methoxy-5-chlorobenzoyl)-propionic acid was effected as described previously (*loc. cit.*). Yield of the lactone was 40 to 55%. The compounds are tabulated in Tables I and II.

TABLE I

PA denotes β-(2-methoxy-5-chlorobenzoyl)-propionic acid.
P'A ,, β-(2-hydroxy-5-chlorobenzoyl)-propionic acid.

No.	Name of the compound.	Formula.	Properties.	% Chlorine. Found.	Calc.
1.	α-Methyl-β-PA	$C_{12}H_{13}O_4Cl$	Needles from hot water, m.p. 120°.	14.0 (255.0)	13.8 (256.5)
2.	Ethyl ester of (1)	$C_{14}H_{17}O_4Cl$	Liquid, b.p. 213-18°/10 mm. n_D^{28}, 1.536.	12.8	12.4
3.	2:4-D.N.P. of (1)	$C_{18}H_{17}O_7N_4Cl$	Yellow needles from alcohol, m.p. 178°.	8.3	8.1
4.	α-Ethyl-β-PA	$C_{12}H_{13}O_4Cl$	Small needles from dil. alcohol, m.p. 147°.	14.1	13.8
5.	α-Ethyl-PA	$C_{13}H_{15}O_4Cl$	Needles from hot water, m.p. 105°.	13.3 (272.5)	13.1% (270.5)
6.	Ethyl ester of (5)	$C_{15}H_{19}O_4Cl$	Liquid, b.p. 217-22/10 mm. n_D^{28}, 1.529.	12 1	11.9
7.	2:4-D.N. P. of (5)	$C_{19}H_{19}O_7N_4Cl$	Yellow needles from alcohol, m.p. 190°.	8.1	7.9
8.	α-*n*-Propyl-P'A	$C_{13}H_{15}O_4Cl$	Needles from hot water, m.p. 118°.	13.0	13.1
9.	α-*n*-Propyl-PA	$C_{14}H_{17}O_4Cl$	White granules from petroleum ether, m.p. 92°.	12.6 (286.0)	12.5 (284.5)
10.	Ethyl ester of (9)	$C_{16}H_{21}O_4Cl$	Liquid, b.p. 187-92°/1 mm. n_D^{30}, 1.516.	11.6	11.4
11.	2:4-D.N.P. of (9)	$C_{20}H_{21}O_7N_4Cl$	Yellow needles from alcohol, m.p. 183°.	7.8	7.6

TABLE I (contd.)

No.	Name of the compound.	Formula.	Properties.	Chlorine. Found.	Chlorine. Calc.
12.	α-*n*-Butyl-P'A	$C_{14}H_{17}O_4Cl$	Needles from hot water, m.p. 168°.	12.7	12.5
13.	α-*n*-Butyl-PA	$C_{15}H_{19}O_4Cl$	White granules from pet. ether, m.p. 95°	12.1 (297.0)	11.9 (298.5)
14.	Ethyl ester of (13)	$C_{17}H_{23}O_4Cl$	Liquid, b.p. 195-200°/3.5 mm. n_D^{28},1.516.	10.9	10.9
15.	2:4-D.N.P. of (13)	$C_{21}H_{23}O_7N_4Cl$	Yellow needles from alcohol, m.p. 205°.	7.7	7.4
16.	α-*n*-Hexyl-PA	$C_{17}H_{23}O_4Cl$	Needles from benzene-petrol, m.p. 114°.	11.0 (328 1)	10.9 (326.5)
17.	Ethyl ester of (16)	$C_{19}H_{27}O_4Cl$	Liquid, b.p. 140-45°/7 mm. n_D^{28}, 1.468.	10.3	10.0
18.	2:4 D.N.P. of (16)	$C_{23}H_{27}O_7N_4Cl$	Yellow needles from alcohol, m.p. 192°.	6.8	7.0

N.B. D.N.P denotes dinitrophenylhydrazone.
Figures in parentheses in last two columns refer to equiv. wt.

TABLE II

No.	Alkyl γ-(2-methoxy-5-chlorophenyl)-butyro lactones.	Formula.	Properties.	% Chlorine. Found.	% Chlorine. Calc.	Eq. weights. Found.	Eq. weights. Calc.
1.	α-Methyl-	$C_{12}H_{13}O_3Cl$	Liquid, b.p. 202-207°/6 mm. n_D^{28}, 1.556	14.8	14.8	238.2	240.5
2.	α-Ethyl	$C_{13}H_{15}O_3Cl$	Liquid, b.p. 227-32°/9 mm. n_D^{28}, 1.545	14.2	14.0	255.7	254.5
3.	α-*n*-Propyl	$C_{14}H_{17}O_3Cl$	Liquid, b.p. 210-15°/2 mm. n_D^{28}, 1.548	13.5	13.2	266.3	268.5
4.	α-*n*-Butyl	$C_{15}H_{19}O_3Cl$	Liquid b.p. 175-80°/3 5 mm. n_D^{28}, 1.547	12.6	12.6	280.6	282.2
5.	α-*n*-Hexyl	$C_{17}H_{23}O_3Cl$	Plates from dilute alcohol, m p. 85°.	11 5	11.4	312.1	310.5

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SHORT NOTES

VOLUMETRIC ESTIMATION OF SILVER

By S. V. Suryanarayana, A.K. Bose and H.N. Das Gupta

In the present communication a simple modified volumetric method for the estimation of silver with the aid of common reagents has been suggested. The process consists in precipitation of silver with potassium iodide in presence of hydrogen peroxide and starch solution. The excess of potassium iodide reacts with hydrogen peroxide to liberate iodine, when the last trace of silver has been precipitated. The liberated iodine produces the characteristic blue colour with starch solution. It will be apparent from the experimental results that changes in the concentration either of the standard solution or of the silver salt, have no influence on the progress of titration. No interference due to the presence of copper in small quantity, zinc, lead, dilute nitric acid, dilute sulphuric acid and oxalic has been observed yet.

Procedure.—The silver salt solution is acidified with 10-20 c.c. of 1:5 H_2SO_4 and to this 5 to 10 c.c. of H_2O_2 (20 vol.) and 2 c.c. of 1% starch solution are added. The solution is then titrated with the standard potassium iodide solution. The end-point is indicated by the blue colour of starch-iodine complex.

The experimental results of a few analyses, according to the present method, are shown in Table I. It also includes the results obtained by the adoption of Volhard's method. It will be evident from the table that results are quite comparable.

Table I

Estimation of silver.

Ag found by the present method.					
0.01N−KI		0.0985N−KI		0.1N−KI	
4.14 mg.	(4.18)mg.	108.4 mg.	(108.4)mg.	107.9 mg.	(107.9)mg.
5.01	(5.05)	54.2	(54.6)	54.0	(54.5)
4.50	(4.48)	216.8	(216.8)	215.8	(216.2)

Figures in parentheses were obtained by Volhard's method.

Further work aiming at studying the influence of interfering substances listed by Hillebrand and Lundell (App. Inorganic Analysis, Rev. Ed., 1953, p. 208) are in progress. It is also proposed to study the suitability of the process in place of assay procedures.

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OLEANOLIC ACID FROM *ACHYRANTHES ASPERA* LINN.

By Hari Narayan Khastgir and Pasupati Sen Gupta

The Indian shrub *Achyranthes aspera* Linn. (Sanskrit : Apamarga) of N. O. Amarantaceae has found use in the Ayurvedic system of medicine against various diseases. The juice of the plant has diuretic and antispasmodic properties. The seeds of the plant were first investigated by Gopalachari and Dhar (*J. Sci. Ind. Res.*, 1952, **11B**, 209) who isolated a sapogenin, $C_{29}H_{46}O$, m.p. 305·6°, and a hydrocarbon, m.p. 64-65°. The authors did not suggest anything about the structure of the sapogenin except the observation that it formed a monoacetate, m.p. 298-300° and gave colour reactions of steroids. More recently Basu *et al.* (*J. Proc. Inst. Chem., India*, 1957, **29**, 55, 73, 161) reported the isolation of a nitrogeneous compound, $C_6H_{11}O_2N$, H_2O, m.p. 292-3°, from the aqueous extract of the entire plant and they named this compound 'achyranthine'. These workers, however, failed to detect the presence of any glycoside in the plant.

We were interested in the study of the glycosidic fraction of the roots of the shrub. In this communication isolation of oleanolic acid from the glycosidic fraction of the roots is described. The defatted alcoholic extract of the dried roots of the plant was hydrolysed with alcoholic dilute hydrochloric acid and the aglycone fraction was purified by extraction with ether, conversion into the water-insoluble potassium salt and again extraction with ether after acidification. The acid, thus obtained, was converted into the acetate, which was found to be identical with oleanolic acid acetate.

Besides oleanolic acid, no appreciable amounts of any other aglycone could be detected.

Isolation of Oleanolic Acid.—Dried and powdered roots of *Achyranthes aspera* Linn. (670 g.) were extracted for 30 hours in a Soxhlet apparatus with 95% ethyl alcohol. The extract was concentrated to a thick syrup and shaken with 200 c.c. of petroleum ether (b. p. 60-80°). The petroleum ether layer was decanted and the residual glycosidic syrup was further washed thrice with similar 200 c.c. portions of petroleum ether. The dark brown glycosidic residue was dissolved in 100 c.c. of 99% ethyl alcohol and 50 c.c. of water and the solution was refluxed for 4 hours after the addition of 75 c.c. of HCl (conc.). The mixture was cooled, diluted with water and filtered. The filtrate was rejected ; the solid residue was washed with water till neutral and then air-dried. The solid was then extracted with ether in a Soxhlet apparatus for 4 hours. The ethereal solution was shaken with 50 c.c. portions of 3% aqueous potassium hydroxide solution and the precipitated potassium salt was filtered off. The ether solution was washed with cold water and evaporated when a very small amount of a tarry neutral product was obtained, which did not yield any crystalline material even after chromatography over alumina.

The aqueous mother-liquor, after the filtration of the solid potassium salt, was acidified with HCl (cold and dilute), when a small amount of a gummy material was precipitated. This gumy acidic material also did not yield any crystalline compound.

Finally, the solid potassium salt was suspended in cold water, acidified with HCl (cold and dilute) and extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulphate and evaporated, when 0.8 g. of a faintly yellow solid, m.p. 2 -98°, was obtained. On repeated crystallisation from methanol and then from acetone the acid melted at 302-304°, $[\alpha]_D$ + 79°. These constants agree well with those of oleanolic acid reported by Djerassi and Lippman (*J. Amer. Chem. Soc.*, 1954, **76**, 5780).

The *acetate* of the above acid was prepared in the usual manner by treatment with acetic anhydride and pyridine. The acetate after several crystallisations from methanol and then from acetone, melted at 261-64°, $[\alpha]_D$ + 77° (reported m.p. 262-65°, $[\alpha]_D$ + 77.6°, *loc. cit.*). The acetate did not depress the m.p. of an authentic specimen of oleanolic acid acetate and the infra-red spectrum of our acetate was identical with that of the authentic specimen. (Found: C, 77.40; H, 10.10. Calc. for $C_{32}H_{50}O_4$: C, 77.06; H, 10.11%).

The authors are indebted to Robert R. Engle of Wayne State University, Michigan, U.S.A. for kindly running the infra-red spectra and to Dr. Carl Djerassi for kindly supplying the authentic specimen of oleanolic acid acetate.

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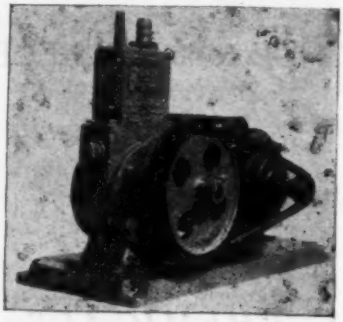

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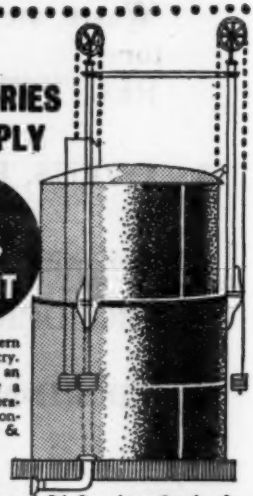

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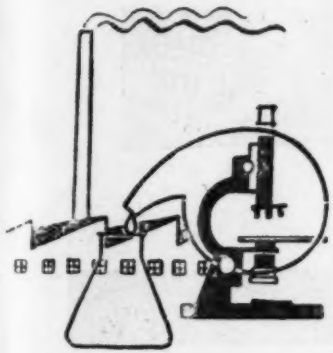

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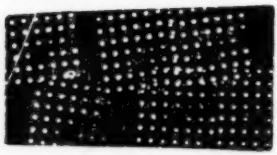

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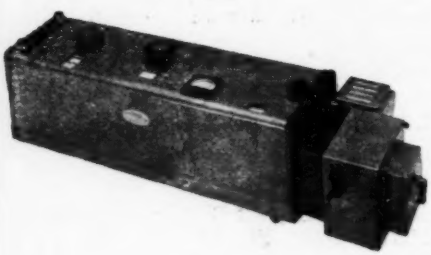

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